



# INVESTIGATION REPORT

Draft Report for Public Comment

## E.I. DUPONT DE NEMOURS & Co., INC.

BELLE, WEST VIRGINIA



### METHYL CHLORIDE RELEASE JANUARY 22, 2010

### OLEUM RELEASE JANUARY 23, 2010

### PHOSGENE RELEASE JANUARY 23, 2010

One Fatality

One Confirmed Exposure

One Possible Exposure

#### KEY ISSUES:

- MECHANICAL INTEGRITY
- ALARM MANAGEMENT
- OPERATING PROCEDURES
- COMPANY EMERGENCY RESPONSE & NOTIFICATION

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## List of Acronyms and Abbreviations

ACC	American Chemistry Council
ALOHA	Area Locations of Hazardous Atmospheres
CFR	Code of Federal Regulations
Cl <sub>2</sub>	Chlorine
CMMS	Computerized Maintenance Management System
CO	Carbon Monoxide
CSB	U.S. Chemical Safety and Hazard Investigation Board
DCS	distributed control system
DMA	dimethylamine
DMS	dimethylsulfate
ECF	ethyl chloroformate
FRC	flame resistant clothing
EPA	U.S. Environmental Protection Agency
GIS	Graphical Information System
HCl	hydrochloric acid
KCEAA	Kanawha County Emergency Ambulance Authority
KPEPC	Kanawha-Putnam County Emergency Planning Committee
LDAR	Leak Detection and Repair
MM	million (old notation style)
MOC	Management of Change
NDE	non-destructive examination
NIMS	National Incident Management System
NIOSH	National Institute for Occupational Safety and Health
NOAA	National Oceanic and Atmospheric Administration
NPS	nominal pipe size
OSHA	U.S. Department of Labor, Occupational Safety and Health Administration
OTPT	Oleum Tower Pump Tank
PHA	Process Hazard Analysis
ppm	parts per million
psig	pound-force per square inch gauge
PSM	OSHA Process Safety Management Standard (29 CFR 1910.119)
PTFE	polytetrafluoroethylene

RMP	Risk Management Plan
RQ	reportable quantity
SAP	System Application & Products
SAR	Spent Acid Recovery Unit
SCBA	self-contained breathing apparatus
SLM	Small Lots Manufacturing Unit
SOPs	Standard Operating Procedures
TQ	threshold quantity
TWA	time-weighted average
VOC	volatile organic compounds

## Executive Summary

On January 22 and 23, 2010, three separate incidents at the DuPont plant in Belle, WV, involving releases of methyl chloride, oleum, and phosgene, triggered notification of outside emergency response agencies.

The incident involving the release of phosgene gas led to the fatal exposure of a worker performing routine duties in an area where phosgene cylinders were stored and used.

Operators discovered the first incident, the release of methyl chloride, the morning of January 22, 2010, when an alarm sounded on the plant's distributed control system monitor. They confirmed that a release had occurred and that methyl chloride was venting to the atmosphere. Managers assessing the release estimated that more than 2,000 pounds of methyl chloride might have been released over the preceding 5 days.

The oleum release, the second incident, occurred on the morning of January 23, 2010. Workers discovered a leak in an overhead oleum sample pipe that was allowing a fuming cloud of oleum to escape to the atmosphere. The plant fire brigade was called and after donning the appropriate personal protective equipment, closed a valve that stopped the leak about an hour after it was discovered. No injuries occurred, but the plant called the Belle Volunteer Fire Department to assist.

The third incident, a phosgene release, occurred later that same day when a hose used to transfer phosgene from a 1-ton cylinder to a process catastrophically failed and sprayed a worker in the face while he was checking the weight of the phosgene cylinder. The employee, who was alone when exposed, was assisted by co-workers who immediately responded to his call for help. Initial assessments by the plant's occupational health nurse indicated that the worker showed no symptoms of exposure prior to transport to the hospital for observation and treatment. A delayed onset of symptoms, consistent with information in phosgene exposure literature, occurred after his arrival at the hospital and his condition deteriorated over the next day. He died from his exposure the next night.



Communication related to emergency notification and response was an issue in two of the incidents and was addressed in conducting the investigation.

At the request of the Board, the U.S. Chemical Safety and Hazard Investigation Board (CSB) investigation team examined all three incidents at Belle due to the severity and potential for even greater consequences, and to examine how and why they could occur at a DuPont facility. DuPont retains stature as an industry leader in the advancement of health and safety practices and develops sound, respected, and widely used safe practice guidance. With such a reputation, the CSB was interested in examining the conditions at the Belle facility that led to a decline in adherence to the higher standard of performance that the corporation historically held.

The CSB incident investigation determined root and contributing causes for each of the three incidents.

An overall analysis revealed common deficiencies in the following management systems:

- Maintenance and inspections
- Alarm recognition and management
- Incident investigation
- Emergency response and communications
- Hazard recognition

The CSB found that each incident was preceded by an event or multiple events that triggered internal incident investigations by DuPont, which investigated all of these precursor events and issued recommendations and corrective actions. Despite investigating these preceding events the recommendations and corrective actions did not prevent the occurrence of similar events.

Because of recent changes to the Kanawha County Metro 9-1-1 response policies and procedures that could lead to delays in treatment for future incidents, the CSB investigators also examined concerns

raised by the emergency response organizations. These concerns included the timeliness and quality of information provided to dispatchers and EMS personnel who responded to two of the incidents and mirrored issues identified in the CSB Bayer CropScience August 2008 incident investigation.<sup>1</sup>

The CSB identified the following root causes:

#### Methyl Chloride Incident (January 22, 2010, 5:02 AM)

- DuPont management, following their Management of Change process approved a design for the rupture disc alarm system that lacked sufficient reliability to advise operators of a flammable methyl chloride release.

#### Oleum Release Incident (January 23, 2010, 7:40 AM)

- Corrosion under the insulation caused a small leak in the oleum pipe.

#### Phosgene Incident (January 23, 2010, 1:45 PM)

- DuPont's phosgene hazard awareness program was deficient in ensuring that operating personnel were aware of the hazards associated with trapping liquid phosgene in transfer hoses.
- DuPont relied on a maintenance software program that was subject to changes without authorization or review and did not automatically initiate a change-out of phosgene hoses at the prescribed interval, nor did they provide a back-up process to ensure timely change-out of aging hoses.
- DuPont Belle's near-miss reporting process was not rigorous enough to ensure that the near failure of a similar phosgene transfer hose, just hours prior to the exposure incident would be immediately brought to the attention of plant supervisors and managers.

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<sup>1</sup> CSB-2008-I-WV (Bayer CropScience)

- DuPont lacked a dedicated radio/telephone system and emergency notification process to convey the nature of an emergency at the Belle plant, thereby restricting the ability of personnel to provide timely and quality information to emergency responders.

The CSB makes recommendations to

- Occupational Safety and Health Administration (OSHA)
- DuPont Belle, WV, plant
- E.I. DuPont de Nemours & Co., Inc.
- Compressed Gas Association of America (CGA)
- American Chemistry Council (ACC) Phosgene Panel

## 1.0 Introduction

### 1.1 Background

At 5:02 a.m. on Friday, January 22, 2010, a release of methyl chloride activated an alarm in the F3455 unit control room, signaling the first of three incidents that would occur over the next 33 hours at the DuPont Belle, WV, facility. No injuries were associated with this incident, but the release went undetected for as long as 5 days. DuPont estimates that more than 2,000 pounds of methyl chloride released to the atmosphere.

At 7:55 a.m. on Saturday, January 23, 2010, a contractor reported seeing a fuming plume on a one-inch diameter sample pipe in the Spent Acid Recovery (SAR) unit. Operations personnel confirmed that oleum was leaking; thus, a fume alert was activated for the entire Belle plant. Plant fire brigade members responded to the release and closed valves that stopped the leak at about 8:26 a.m., after which the “all clear” was sounded.

The third incident occurred just 6 hours later. At approximately 1:45 p.m., an operator walked into the phosgene cylinder storage area in the Small Lots Manufacturing unit and was sprayed in the face and upper torso with phosgene when a flexible hose suddenly ruptured. The worker called for assistance and coworkers immediately went to his aid. His personal dosimeter indicated that he had been exposed to a significant dose of phosgene but he did not exhibit immediate signs of breathing problems. About 3 hours after arriving at the hospital his condition deteriorated, and he died the following night.

No injuries occurred as a result of the first two releases, but communication to Metro 9-1-1 dispatchers regarding the nature of the each release on Saturday became an issue post-incident. CSB investigators examined how information related to the incidents was conveyed to Metro 9-1-1 dispatchers. The CSB also interviewed Kanawha County Ambulance Authority (KCEAA), Kanawha-Putnam Emergency Planning Committee (KPEPC), and Metro 9-1-1 representatives to assess each incident and determine if

actions could be taken to improve communication methods to prevent recurrence of the issues brought to the attention of county officials. During the Saturday afternoon call for assistance from DuPont, Metro 9-1-1 dispatchers were not provided with sufficient information regarding the nature of the emergency and the chemicals involved to adequately inform the responding EMS personnel. Many of those interviewed were familiar with the role of the CSB, having participated in conferences and interviews as part of the CSB's investigation of the August, 2008 Bayer CropScience incident in attempts to address similar emergency response and notification issues.

Because of recurring communication problems associated with emergency responses to chemical plants in the Kanawha Valley, responding medical units have established a practice of not immediately going onto a property that has called for assistance. Instead, EMS personnel respond to a staging area as far as a mile away where they remain until they receive more detailed information regarding the material involved and whether the victim has been, or will need to be decontaminated prior to transport to a hospital. This practice was developed by the emergency response organizations due to information that was sometimes so imprecise that EMS personnel could not ensure that they or their equipment would not be contaminated by a hazardous chemical as a result of transporting an exposed victim.

In examining the activities of employees involved in the response, the CSB learned that two other DuPont employees were also possibly exposed to phosgene. One coworker noticed that his dosimeter was discolored, indicating exposure, after he transported the victim part of the way to the plant medical center in a company truck. He transferred the victim to the care of a supervisor who completed the trip to the medical center with the victim. The second exposure occurred when a worker, unaware of the phosgene release, went into the area of the phosgene shed and noticed an odor that he had never smelled before. Unsure of what the odor was, he left the area and joined his co-workers in the control room.

## 1.2 Investigative Process

The CSB began monitoring and continued to track information related to the chemical release incidents at the DuPont Belle, WV, facility that were reported to the media and the National Response Center (NRC) throughout the weekend of January 22 and 23, 2010. On January 25, 2010, the CSB board deployed an investigation team. Because of the number and potential for more severe consequences at the DuPont Belle plant over this 2-day period, the CSB launched an investigation to determine the root and contributing causes and to issue recommendations to help prevent similar occurrences. Although the consequences of the first two incidents were not as severe as the third, the CSB decided that since the three incidents occurred in less than 2 days, including one that led to a fatality, all three would be investigated to determine any common causes.

The investigative team arrived at the Belle Plant on January 26, 2010, and met with Occupational Safety and Health Administration (OSHA) inspectors; U.S. Environmental Protection Agency (EPA) officials; and DuPont representatives to explain the CSBs authority and purpose for conducting the investigation.

The CSB investigation team remained onsite for 2 weeks and made subsequent visits to Belle to conduct independent investigations of each of the three DuPont Belle, WV, facility incidents. During its investigations, CSB investigators:

- Interviewed plant personnel, emergency responders, plant supervisors and managers, and corporate personnel;
- Coordinated the examination, removal, and storage of physical evidence;
- Requested and reviewed relevant documentation;
- Reviewed technical and industry guidance, standards, and regulations;
- Discussed emergency response issues with the Kanawha-Putnam Emergency Planning Committee (KPEPC), Kanawha County Emergency Ambulance Authority (KCEAA), and Metro 9-1-1 dispatch center officials;

- Entered into joint testing protocol agreements with DuPont, OSHA, and the EPA;
- Observed metallurgical testing of the oleum sample line;
- Observed metallurgical testing of the phosgene stainless steel overbraid hose; and
- Observed analytical testing and analysis of the polytetrafluoroethylene (PTFE) inner core of the transfer hoses involved in the phosgene release.

## **1.3 E.I. DuPont de Nemours & Co., Inc.**

### **1.3.1 Company History**

E.I. DuPont de Nemours and Company, named after its French founder, Eleuthère Irénée du Pont, was established in 1802 as a gunpowder manufacturing company on the Brandywine River in Wilmington, DE. DuPont grew as a manufacturer of gunpowder and explosives in the United States and a century later, in 1902, transitioned into a science-based chemical company. DuPont established Experimental Station, the first industrial laboratory where researchers and scientists began work on nitrocellulose chemistry and smokeless powders to improve military rifles for the World War I effort. By the 1920s, DuPont purchased several chemical companies and focused on polymers, which led to the discovery of neoprene (synthetic rubbers), polyester, and nylon by 1935. Many of these products were in demand during the Second World War. Further work with plastics and fibers led to the development of Teflon™, Lucite™, Nomex™, and Mylar™ in the 1950s. DuPont also introduced a number of inorganic insecticides and fungicides such as Lannate® (methomyl) and Telvar®, which eventually led to the establishment of its agricultural products business. By the mid-1980s, DuPont had grown to almost 100 major businesses selling a wide range of materials such as textiles, agricultural chemicals, petroleum, and biomedical products.

### **1.3.2 DuPont Business Areas and Corporate Management**

DuPont, headquartered in Wilmington, DE, has 58,000 employees in more than 80 countries. The company offers a broad range of products for industry and consumer use, including pesticides,

electronics, apparel, and biomedical supplies. Five business platforms comprise the DuPont organization: Agriculture and Nutrition, Coatings and Color Technologies, Performance Materials, Electronics and Communications, and Safety and Protection. Within each business platform are strategic business areas<sup>2</sup> focusing on the production, sale, and distribution of products and services related to each marketing area.

The Crop Protection business area, a segment of the Agriculture and Nutrition platform, is responsible for the development, manufacture, and sale of fungicides, herbicides, insecticides, and seed treatments globally. The agriculture industry uses DuPont Crop Protection products on a variety of crops worldwide including cotton, soybeans, fruits, and vegetables. The F3455 and Small Lots Manufacturing (SLM) units at the Belle Plant manufacture intermediate chemicals for their Crop Protection products. In 2009, the Agriculture and Nutrition platform had the most sales of any business area at \$8.3 billion.

A 13-member Board of Directors, including the chairperson and CEO, manage DuPont. Executive committees made up of board members and representatives from DuPont businesses oversee areas such as environmental policy, corporate governance, strategic direction, and auditing. In 2010, DuPont had global sales of \$31.5 billion and ranked as the third-largest chemical company in profits and second in revenues in the world.

### 1.3.3 Safety at DuPont

Concern for safety and health at DuPont became a part of the company's structure in 1805 due to the hazards of gunpowder and explosives production. The early corporate safety program was rooted in process safety concepts more than a century before governing safety regulations existed. Practices such as

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<sup>2</sup> Pioneer Hy-bred, Crop Protection, Nutrition and Health, Electronics and Communications, Performance Coatings, Performance Polymers, Protection Technologies, Building Innovations, Sustainable Solutions, Chemicals and Fluoroproducts, Titanium Technologies, and Applied Biosciences.



safe siting of buildings, explosion venting concepts, incident investigation processes, and emergency response were implemented in the DuPont gunpowder mills throughout the 19th century.

The company continued to focus on health and safety to improve safety performance and in 1915 created the company's first corporate safety division, which was responsible for technical training, safety inspections, project design reviews, and the purchase of safety equipment. According to DuPont incident records, the safety division participation in facility operations decreased incident rates throughout the company. As a result, individual sites established site-specific safety groups in the mid-1930s. Hazard elimination was recognized as a priority above education and personal protection (Klein, 2009).

### 1.3.3.1 Early Process Safety Program

The release of highly toxic methyl isocyanate (MIC) at the Union Carbide Corp. in Bhopal, India, resulted in nearly 3,800 immediate deaths, and 16,000 are estimated to have since died as a result of exposure, while in excess of 100,000 still report associated illnesses. In response to the Union Carbide incident, chemical companies, industry associations, and government agencies directed efforts to decrease process safety risks, which eventually led to the establishment of the OSHA Process Safety Management (PSM) Standard (29 CFR 1910.119) and the creation of the CSB as part of the Clean Air Act amendment of 1990.

Prior to establishing the OSHA PSM Standard, DuPont was practicing many process safety concepts at its facilities as part of the DuPont Process Hazards Management (PHM) Program. After a serious 1965 incident in Louisville, KY caused 12 fatalities, the company directed all sites to perform hazard reviews to evaluate the safety of site processes, which eventually became a corporate Process Hazards Review (PHR) program. The PHR was intended to prevent serious process-related incidents, and each site handling hazardous substances had to have a PHM program.

The Bhopal incident contributed to an increase in DuPont's focus on process hazards management particularly in the manufacture of MIC. DuPont developed an inherently safer method of manufacturing

and handling MIC that eliminated MIC bulk storage as it relied on producing and directly consuming MIC. The company also created the Highly Toxic Materials (HTM) Subcommittee to review the global management of toxic chemicals. In 1985, HTM became a corporate guideline, and a separate subcommittee was established to focus on each of the 15 highly hazardous materials identified within the company. DuPont continued to refine its PHM program, eventually developing professional guidance for process safety and OSHA PSM rulemaking (Mottle et al., 1995).

#### 1.3.3.2 Zero Incident Goal

DuPont introduced the zero incident goal in the early 1900s as a management directive to drive injury rates down to zero through continuous improvement of safety practices. The “zero” concept became a core strategy as the company grew and accepted the philosophy that all injuries, occupational illnesses, and environmental incidents were deemed preventable and that the goal for all was zero.

DuPont became recognized throughout industry as a safety innovator and leader. The company offers services as a safety resource for other corporations to evaluate and improve workplace safety, which include methodologies and technical training to manage and improve employee and contractor health and safety performance as well as process safety improvements.

## 1.4 DuPont Belle Plant



Figure 1. DuPont Belle, WV, facility on the Kanawha River (EPA, 1973)

The DuPont Belle plant is located in Belle, WV, about 8 miles east of Charleston, the state capital. The plant occupies about 723 acres along the Kanawha River and sits in an industrial, commercial, and residential use area. The plant was established in the West Virginia coal country as part of a post-World War I effort to produce ammonia. In the early 1920s DuPont spent \$27 million<sup>3</sup> on a highly complex production facility with atmospheric compressors capable of producing 25 tons of ammonia per day. Belle's high-pressure ammonia technology yielded a host of collateral benefits. Methanol was initially manufactured on a small scale and then rapidly expanded to 1 million gallons a year. By 1935, Belle had

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<sup>3</sup> Equivalent to \$332 million in 2010, according to the Bureau of Labor Statistics Inflation Calculator.

become DuPont's largest facility with more than 80 different chemical products, which included the first synthetic urea used in fertilizers and plastics. In 1939, DuPont began producing nylon chemical intermediates at Belle, and by 1944 the plant was producing 30 million pounds of synthetic polymers per year. Expansion of nitrogen and nylon intermediate production at Belle continued after the war, and new product lines were introduced regularly. In 1969 Belle began producing the fungicide Benlate®. Currently, the DuPont Belle Plant produces a variety of organic chemicals and agricultural intermediates and products. According to company documents, the plant had the best safety record of any DuPont production facility prior to the incidents of January 22 and 23.<sup>4</sup>

In January 2010, the DuPont Belle Plant employed approximately 440 and had seven primary operating divisions occupying a 105-acre manufacturing area nearly 1 mile long. The DuPont-operated SAR unit is owned by Lucite International and operated by DuPont employees. The Belle facility is also the site of the newly constructed Kureha unit, owned by the Kureha Corp. of Japan, which is operated by Kureha employees on DuPont's Belle site. The Kureha production unit uses glycolic acid produced by DuPont as a feedstock for polyglycolic acid, a specialty plastic.

The DuPont Belle plant holds a Resource Conservation and Recovery Act (RCRA) Part B Treatment and Storage Permit for onsite handling of waste materials, in addition to a RCRA-permitted drum storage facility onsite. The Belle plant participates in a Community Action Council (CAC) aimed at addressing citizen concerns regarding site safety, health, and environmental performance. The council is comprised of citizens from neighboring communities and representatives from the industrial facilities in the region.<sup>5</sup>

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<sup>4</sup> [www.2.dupont.com/heritage](http://www.2.dupont.com/heritage).

<sup>5</sup> DuPont Belle Plant Information Sheet.

## 2.0 Methyl Chloride Release (January 22, 2010)

### 2.1 Background

The Belle plant's F3455 unit manufactures the intermediate F3455, a chemical that is shipped to another DuPont facility to make the herbicide Velpar<sup>®</sup>. Due to the exothermic reaction in the first reactor, dissolved methyl chloride vaporizes and normally exits through the reactor vent line along with carbon dioxide, nitrogen, and trace amounts of dimethylamine (DMA) vapor through a process scrubber and then to a thermal oxidizer for emission control. To protect against damage to the scrubber<sup>6</sup> if excessive pressures occur, a piping connection upstream of the vent line is routed to a rupture disc that will burst and allow for venting outside on the roof of the building, which occupies two reactors (Figure 2). However, due to a lack of safety considerations during installation, a 0.5-inch weep hole<sup>7</sup> was placed on the vent line inside the building. As a result, dangerous chemicals vent inside the building if the rupture disc bursts.

Unaware that the rupture disc had blown during a nitrogen purge activity before the reactor startup, plant personnel proceeded with the normal production run. For nearly 5 days, methyl chloride vapor passed through the blown rupture disc and escaped into the operation building and outside atmosphere. On the fifth day, the methyl chloride vapors interfered with the chemical sensor configured to detect ethyl chloroformate (ECF), which alerted the workers.

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<sup>6</sup> A thermal oxidizer is a process unit for air pollution control in many chemical plants that decomposes hazardous gases at a high temperature and releases them into the atmosphere.

<sup>7</sup> In process vent lines that lead to the atmosphere, protection must be installed to prevent ambient moisture -- from rain or other elements -- from collecting within the vent line. One such protection is a "weep hole," which is a small hole drilled into a vent line that allows drainage.

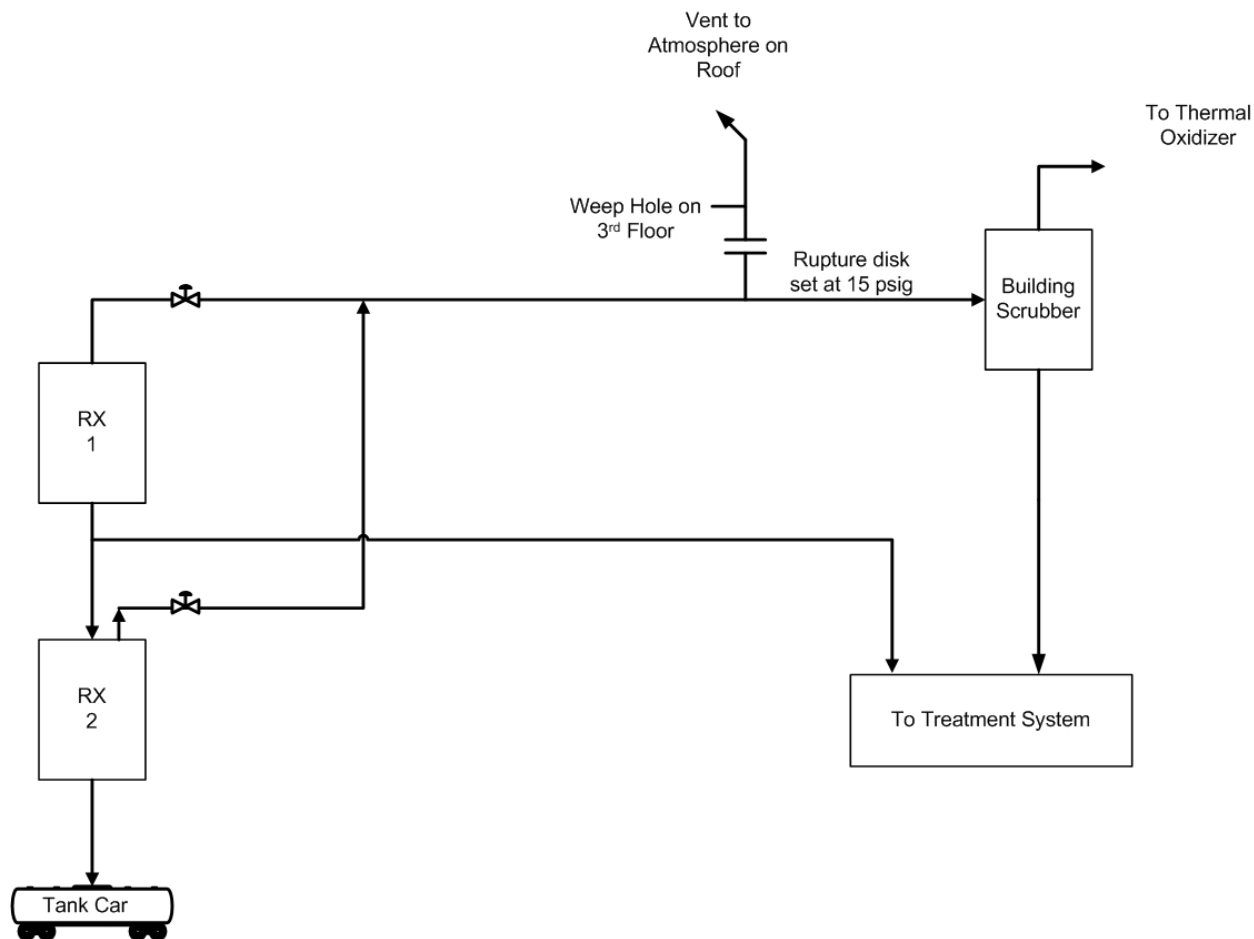


Figure 2. Simplified thermal oxidizer and rupture disc block flow diagram

### 2.1.1 Methyl Chloride

Methyl chloride, also called chloromethane or monochloromethane, is a colorless gas with a faint sweet odor at low concentrations.<sup>8</sup> The odor may not be noticeable and cannot be relied upon as warning of concentrations that are dangerous to health.<sup>9</sup> Methyl chloride is extremely flammable; has a potent

<sup>8</sup> The odor threshold, or concentration, of methyl chloride detectible by most humans varies between 10 and 250 ppm.

<sup>9</sup> [\(http://www.oxy.com/Our\\_Businesses/chemicals/Documents/methyl\\_chloride/Methyl%20Chloride%20Handbook.pdf\)](http://www.oxy.com/Our_Businesses/chemicals/Documents/methyl_chloride/Methyl%20Chloride%20Handbook.pdf).(11/2009)

narcotic effect similar to trichloromethane, also known as chloroform; and is listed as a Group 3 carcinogen<sup>10</sup> by the International Agency for Research on Cancer (IARC). The OSHA 8-hour time-weighted average (TWA) concentration is 100 ppm and the National Institute of Occupational Safety and Health (NIOSH)-designated Immediately Dangerous to Life and Health (IDLH) concentration is 2,000 ppm.

Symptoms of methyl chloride exposure include dizziness, confusion, and nausea, and at higher concentrations, extreme nervousness, trembling, and possible loss of consciousness. High concentrations or long exposure time can be fatal. The gas is also heavier than air and therefore settles close to the ground.

## 2.2 Incident Description

The F3455 process was in the first series of batch runs following an extended maintenance outage from September 12, 2009, through January 17, 2010. The release is thought to have initiated on January 17 during the first batch run in the unit and continued until discovered on January 22; the release rate may have been sporadic throughout this period.

On January 22, 2010, an air monitor alarm on the process control monitor alerted plant operating personnel of a chemical release while they were adding DMA<sup>11</sup> to the reactor. The sensor for this alarm, located on the third floor of the F3455 building, is calibrated to activate when it detects ECF at 0.5 ppm. The methyl chloride vapors interfered with the ECF sensors on the third floor and activated the alarm. The distributed control system (DCS) recorded the alarm at 5:02 a.m., and responding operators saw a

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<sup>10</sup> Substances the IARC lists as Group 3 carcinogens are mixtures or agents for which evidence of carcinogenicity in humans is inadequate and limited in experimental animals.

<sup>11</sup> Dimethylamine (DMA) is a toxic and extremely flammable, colorless product with a fishy or ammonia-like odor. DMA attacks the respiratory system and irritates eyes and skin and at higher concentrations can cause pulmonary edema. The OSHA 8-hour TWA is 10 ppm and the NIOSH IDLH is 500 ppm. Humans can detect DMA odors at 0.34 ppm (Sittig, 2008). DMA is a heavier than air vapor and settles close the ground

diffused fog and a liquid puddle near a 0.5-inch nominal pipe size (NPS) vent/drain pipe referred to as a weep hole (Figure 3). This connection was associated with a thermal oxidizer “vent stack,” which, vents to the atmosphere on the roof of the building under normal operation. Operators notified the board operator at 5:19 a.m. when they found the source of the release.

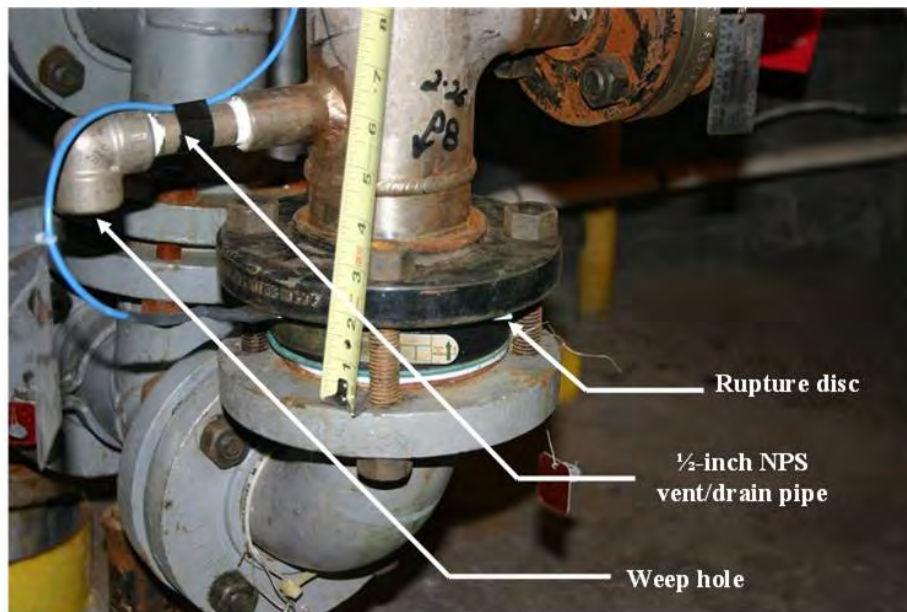


Figure 3. 0.5-inch NPS vent/drain pipe and rupture disc

### 2.2.1 ECF Sensor Alarm

The ECF sensor was chlorine detecting, not ECF. The ECF sensor is responsive to chemicals composed of chlorine (i.e. ethyl-*chloroformate* [ECF] and methyl-*chloride*). On the fifth day, the chlorides present in the release were of sufficient concentration near the ECF sensor to activate the alarm.

### 2.2.2 Odor Detection Considerations

The methyl chloride, DMA and HCl mixture is extremely odorous, however, due to the nature of the F3455 process, operating personnel would have had to be in the area of the 0.5-inch weep hole at the time of the release to see or smell the leak.



Methyl chloride liberated during this phase of the reaction would have likely taken the normal route to the thermal oxidizer piping, where it would have been consumed and vented to the atmosphere unnoticed.

The vent releases products of the reaction into the room only if the pressure inside the pipe is greater than the pressure in the room.

The rupture disc piping was routed to the atmosphere above the roof of the building, which would have provided an outlet path for the methyl chloride vapor where it would have dissipated and dispersed without notice.

The day before the leak was discovered, a crew performed a leak detection and repair (LDAR)<sup>12</sup> inspection on the third floor of the building near the location of the release. The volatile organic compounds (VOC) electronic monitor was calibrated to detect methyl chloride, ECF, DMA, and methanol. Although an area within 12 inches of the weep hole for the rupture disc was checked for leaks with the device, it did not detect any VOCs.

### 2.2.3 Incident Response

In response to the ECF alarm, operators took a VOC analyzer to search for the source of the vapor and immediately smelled an offensive odor on the third floor of the building. They observed steam-like fumes near the vent pipe and dripping liquid accumulating in a puddle on the floor, both clear indications that the rupture disc had burst (Figure 4). The operators left the process area, closed all valves leading to the vent line, and cooled the reactors to stop the process. At about 9:30 a.m. maintenance mechanics replaced the rupture disc and burst sensor.

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<sup>12</sup> The Clean Air Act requires refineries and chemical plants to develop and implement a LDAR program to control fugitive emissions. Fugitive emissions occur from leaks on valves, pumps, compressors, pressure relief valves, flanges, connectors, and other piping components.

After receiving confirmation of the release, the board operator notified the process supervisor who then calculated the estimated duration and magnitude of the release. After performing these calculations, the supervisor notified the plant manager, the safety health and environmental (SHE) manager, the area manager, and the unit technology leader and advised them that the release may have been ongoing for the entire run of 9 batches, which took place over 5 days. DuPont estimated that approximately 2,000<sup>13</sup> pounds of methyl chloride were likely released to the atmosphere.

During the initial phases of the DuPont incident investigation, employees discovered that the burst sensor on the rupture disc had started alarming 5 days prior to the incident. Due to its history of unreliability, operators likely became desensitized to the alarm indicating that the rupture disk had burst. This was the first incident in this sequence of events that led to a safety pause<sup>14</sup> at the plant.

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<sup>13</sup> DuPont, in its final investigation report, determined that 2,045 pounds of methyl chloride and 25 pounds of HCl released to the atmosphere as a result of this incident.

<sup>14</sup> A safety pause is a structured work stoppage that the plant manager initiates to engage the entire work force with the objectives of increasing awareness of hazards, providing safety education, and addressing past incidents. A safety pause was initiated at the Belle facility on Saturday, January 23, 2010, because of the incidents at the F3455 and SAR Units.



Figure 4. Rupture disc piping and vent pipeline to atmosphere on roof

Once it determined that the release quantity was in excess of the CERCLA reportable quantity (RQ) of 100 pounds<sup>15</sup>, in compliance with Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) of 1980, DuPont reported the release of methyl chloride to the NRC DuPont also reported the release to the WV State Department of Homeland Security Emergency Operations Center, who then notified the U.S. Coast Guard. Kanawha County Metro 9-1-1 was not informed of the release until 2:00 p.m. on January 22, 2010, nine hours after discovery.

## 2.2.4 Community Impact

DuPont estimated that between January 17 and 22, 2010, 2,045 pounds of methyl chloride; 25 pounds of hydrogen chloride; and trace amounts of DMA released to the atmosphere through a vent line on the roof of the F3455 building. No monitoring information was available to determine the concentrations of chemicals released to the atmosphere through the vent line. If monitoring information had been recorded, a more accurate estimate of chemical concentration would have provided data related to when the release first started and the potential for off-site impact. No workers at the facility reported any symptoms from methyl chloride or any of the other toxic chemicals either during or after the release. DuPont did not receive any odor complaints from the community.

## 2.3 Incident Analysis

### 2.3.1 Mechanical Integrity

Rupture discs are overpressure protection devices used in processes operating above ambient pressure. They are intended to prevent equipment damage including catastrophic failure. Without them, a process upset can cause unsafe levels of pressure in a system and cause an overpressure incident. Since these devices activate only when a system has had an overpressure event, it is imperative that their activation be

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<sup>15</sup> Under CERCLA, operators of facilities and vessels are required to immediately report releases above the EPA RQ to the NRC.

discovered. In this application, it releases hazardous chemicals to the atmosphere. One approach to assist early detection is to evaluate the alarm management process and, where appropriate, adjust process parameters so that an alarm will activate prior to the disc actually bursting. Another strategy is to evaluate the process and eliminate the conditions that are causing the pressure to rise to levels that would cause the disc to burst. Regardless, once systems have been selected, the configuration should be reviewed by a team including process engineers, control engineers, and operations managers (Lees, 2005).

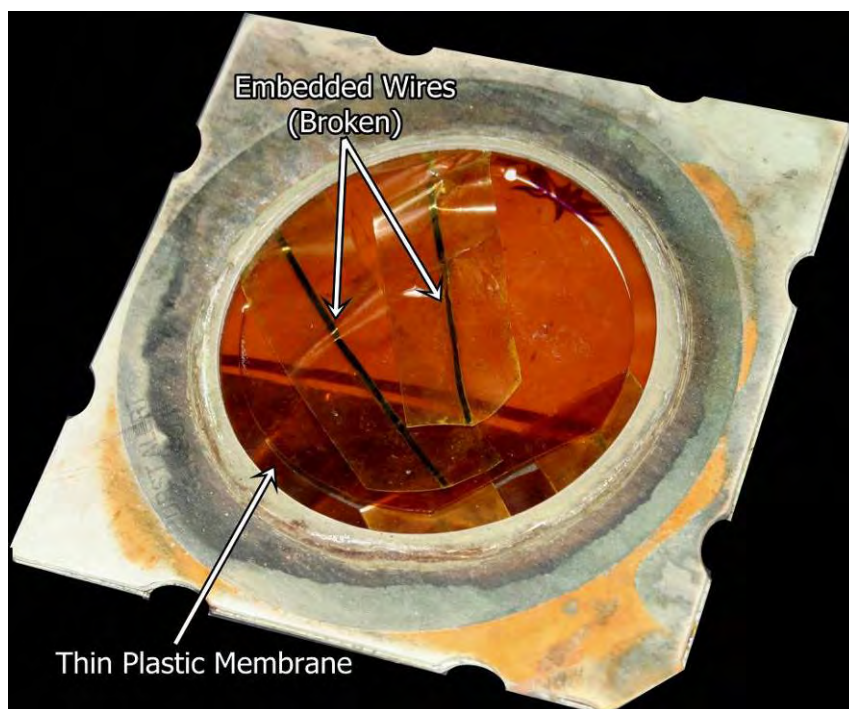


Figure 5. Rupture disc burst sensor post-incident

DuPont Belle used a “burst sensor” intended to notify the board operator that the rupture disk (Figure 5) activated. A burst sensor is a thin plastic membrane with embedded wires installed on top of the rupture disc. Small electrical current passes through the wires. If the rupture disc activates, it breaks the membrane and embedded wires and triggering the alarm.

The CSB learned that the rupture discs and sensors associated with this system were historically problematic. The burst sensor involved in the January 22, 2010, incident had been replaced many times

because it was not reliable. Initially the sensor was battery-operated, sending signals to a remote receiver in the control room rather than to the process control monitor. However, operators found that the battery life on the sensor was short; consequently, they received frequent false, or “nuisance,” alarms. According to Management of Change (MOC) documentation, “... the burst sensor [was] in and out of alarm every 3 minutes.” When the batteries failed, the transmitter sent an alarm to the remote receiver to notify the operators. This device displayed the same alarm text as when the sensor detected a burst rupture disc. Because the batteries needed frequent replacing, and because the operators had to wait for an electrician to change the batteries, the false alarms became a nuisance.

Battery life, however, was not the only reported shortcoming of burst sensors. Operators told CSB investigators that burst sensors were so delicate that they could sometimes tear during the installation and that liquid condensation on top of the sensors sometimes caused them to fail and trigger a false alarm.

An improved burst sensor indicator was installed on the DCS while the unit was down for maintenance just before the incident. Operators indicated they were not retrained to respond to the more reliable burst sensor alarm and still considered it a nuisance.

### 2.3.2 Design and Maintenance of Rupture Discs

The rupture disc involved in the incident was a 4-inch diameter graphite rupture disc, designed to rupture at 15 psig, and mounted in neoprene casing (Figure 6). While the rupture disc is on a preventive maintenance (PM) schedule, the annual frequency was so infrequent that the disc is only replaced when it has activated or when it is removed for certain processes. Operators told CSB investigators that once removed, the rupture discs, intact or compromised, are thrown away and are replaced with new ones.

Even without a burst sensor, all overpressure protection devices, including rupture discs, should be routinely checked on an effective PM schedule as a layer of protection.<sup>16</sup>

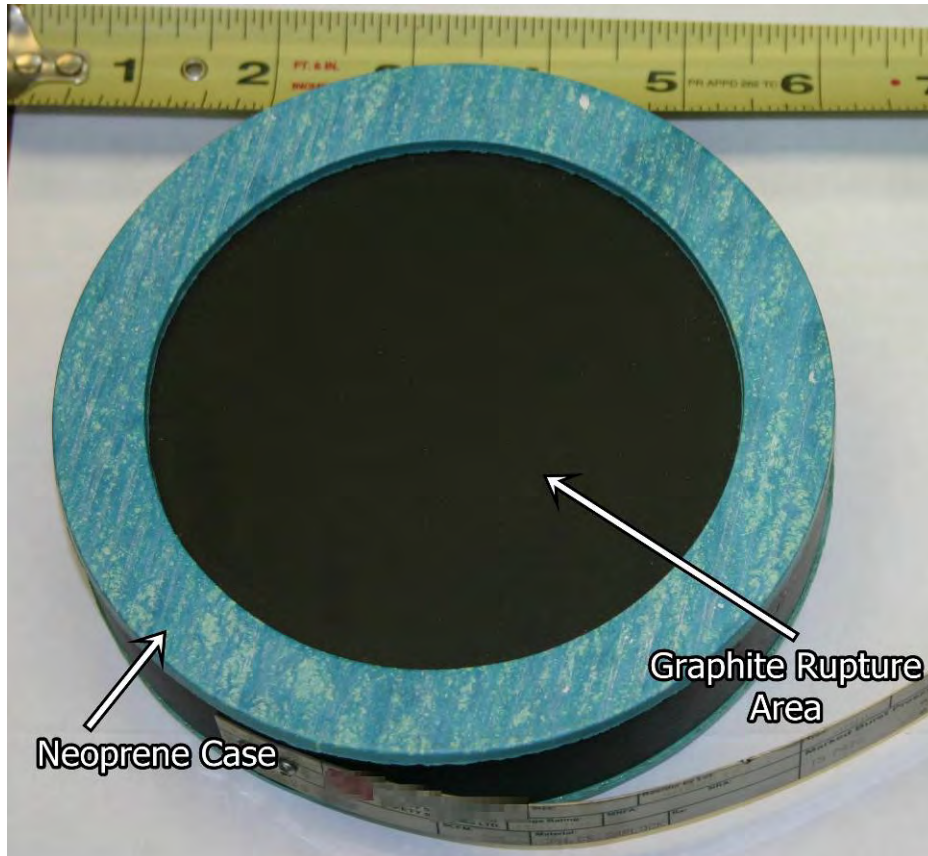


Figure 6. New rupture disc

### 2.3.3 Previous Incidents of Rupture Discs Bursting

Since 2005, the rupture disc on the F3455 unit vent line had experienced nine recorded activations. On April 11, 2006, the rupture disc activated three times. DuPont determined that the disc was most likely experiencing thermal or hydraulic shock. Thermal shock would occur from boiling reactor vapor mixing

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<sup>16</sup> BS&B Safety Systems, Inc, *Special Applications and Preventive Maintenance*, Catalog 77-1007, Section B.

with cool liquid on the disc due to its close proximity to the reactor, hydraulic shock would occur from any “sloshing” in the line upstream of the disc. This recurring problem was remedied by moving the rupture disc a greater distance away from these units and eventually to the third floor of the building toward the extreme end of the vent line.

An incident in May 2006 helps illustrate how the January 22, 2010, release could have gone undetected for 5 days. On May 6, 2006, a rupture disc activation went unnoticed for 48 hours. Although operators complained about strong odors in the F3455 building, they never considered the rupture disc as the source. The operators and supervisory staff identified multiple locations where fugitive emissions could have been producing the offensive smell. Eventually, when a new batch of F3455 was started, an operator near the vent line observed fuming by the rupture disc, which indicated that it was the odor source.

Pipe blockage at the unit was the most commonly reported cause of a premature, rupture disc activation, as shown in Table 1. The F3455 process creates various solids in the vent and process lines, which eventually block flow, increasing the pressure in the system. Once the blockage is melted by the process temperature or forced through the line due to the increased pressure, the resulting pressure spike activates the rupture disc.



Previous Rupture Disc Incidents	
Date	Cause
05/20/05	Unknown
05/31/05	Pressure Control Issues
04/11/06	Hydraulic/Thermal Shock <sup>17</sup>
05/06/06	Blockage <sup>18</sup>
06/16/06	Unknown
05/30/07	Ruptured during Water Cleaning
06/12/07	Blockage
04/15/08	Blockage
02/24/09	Blockage

Table 1. Previous rupture disc events in the F3455 unit

### 2.3.4 Management of Change--Technology and Subtle Change

Within DuPont, Management of Change (MOC) procedures are defined at a corporate level and adopted according to each site’s procedures. At the corporate level, the PSM Standard defines two types of MOC: technology (MOC-T) and subtle changes. MOC-T is defined as “a change in hazards of materials (including the introduction of chemicals), a change in equipment design basis, or a change to the process design basis.” Subtle changes are defined as “any change within the documented [process technology] that is not a replacement in kind.”<sup>19</sup> The corporate PSM Standard gives subtle changes special attention when used in high hazard processes, such as the F3455 and SLM units at the Belle facility. The corporate PSM Standard states, “subtle changes in the field can (and have) led to catastrophic events.” However, even with this knowledge the MOC team at Belle incorrectly categorized the burst sensor installation as a subtle change.

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<sup>17</sup> This incident was actually three incidents over a short period. The rupture disc was discovered ruptured and replaced three times before the unit was shut down for further investigation.

<sup>18</sup> This incident went undiscovered for 48 hours.

<sup>19</sup> The corporate DuPont PSM Standard defines “replacement in kind” as “[the] replacement of an instrument or electrical, piping, or other process equipment component with an identical part or an approved equivalent part that is specified by the applicable DuPont Engineering standard.”

At the Belle site the standard operating procedures (SOPs) do not distinguish between MOC subtle changes and MOC-T. The MOC package documentation, however, shows that subtle, often referred to as “minor,” changes are not subjected to the same in-depth review as a MOC-T. When the MOC is marked as a subtle change, the level of safety review is at the discretion of the MOC team leader.

The MOC package that first installed the rupture disc burst sensor was marked as a subtle change and included a “what if” review that stated, “What if you get a false positive indication (indicating failed disc, but not actually failed)? Not a safety issue. Shut down and investigate.”

This type of review did not go deep enough to confirm that false-positives could lead to a nuisance alarm. A nuisance alarm can create risk by desensitizing operators to a hazard and be more detrimental than the absence of the alarm. In the MOC section marked “Reason for this Type of Safety Review,” the response by the MOC team leader was “Minor Change.”

The MOC package that converted the burst sensor from battery-powered to a supplied power device was also marked as a subtle change. Again, the MOC team leader recorded in the documentation that “a ‘What If’ review [was] appropriate for the afore-mentioned [sic] change.” The MOC did not address the operators’ non-battery related concerns for the burst sensor or how to re-train the board operator to no longer treat the burst sensor alarm as a false-positive.

Because MOC packages deemed “subtle” are not given the same level of review as MOC-T packages, the subtle change MOC packages did not identify or prevent the potential causes of this incident.

### 2.3.5 F3455 Unit Turnaround

On June 6, 2009, nearly 2 years after installing the battery-operated transmitter, DuPont attempted to eliminate the false alarms caused by low batteries by wiring the transmitter to a standard electrical circuit. The unit was shut down during a maintenance turnaround that lasted from September 12, 2009, through January 17, 2010.

During the shutdown, there was significant maintenance activity, including work that, by its nature, triggered alarms, but that did not require response from the operators because there were no “live” process streams that would initiate an actual alarm.

DCS data recorded during the shutdown indicated that the pressure in the reactor system increased slowly from December 18, 2009, to December 20, 2009, when it exceeded the rupture disc rating (Figure 7). The source of the pressure was a nitrogen valve on a level indicator that slowly leaked nitrogen into the system.<sup>20</sup> The rupture disc burst, and the burst sensor triggered an alarm as it should have. Under normal operating conditions, the operators would have investigated to understand, acknowledge, and correct the alarm condition. However, extensive maintenance work was still underway in the unit; thus, the operators did not address the alarm as they would have under normal operation.

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<sup>20</sup> The level instrument measures the difference between the pressure in the vapor space inside the top of the reactor and the pressure under the liquid at the bottom of the reactor. Based on the pressure difference, the control computer calculates the amount of liquid in the reactor. The nitrogen provides a chemical barrier between the reactor liquid and the level instrument.

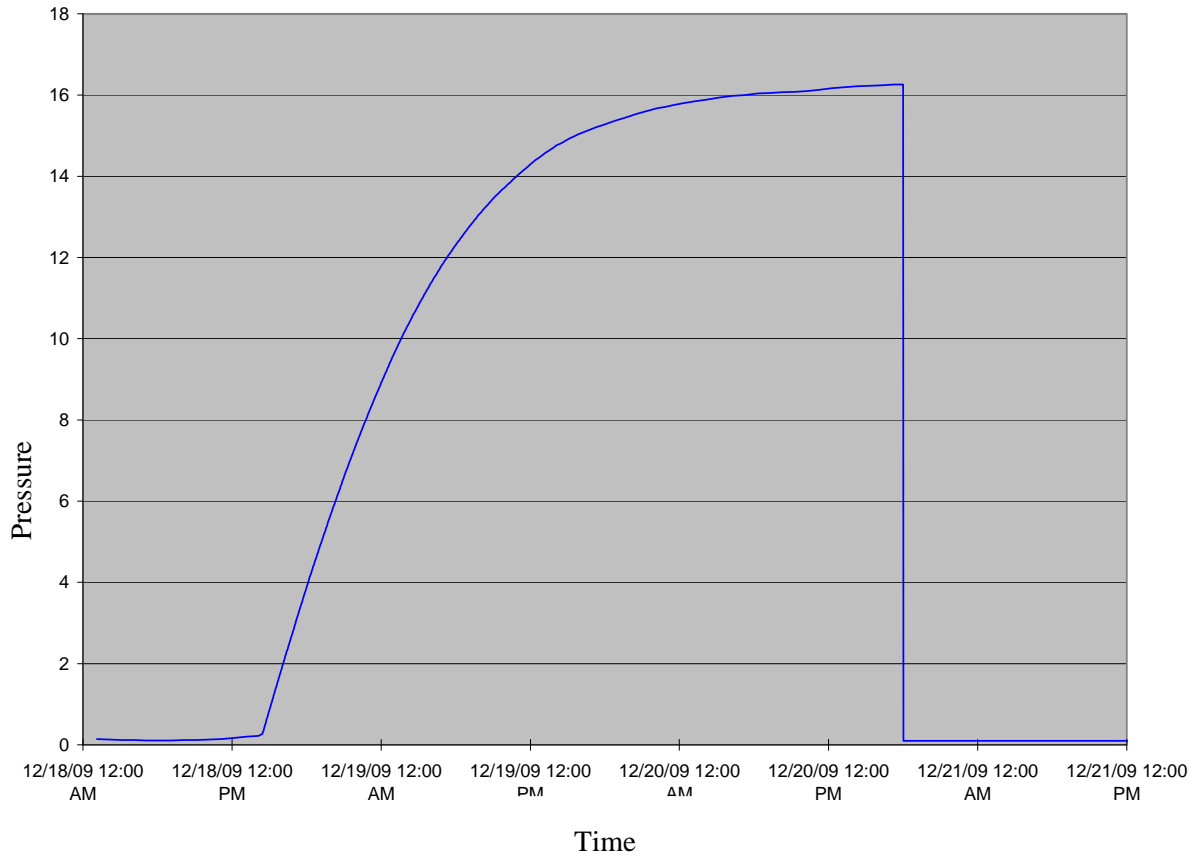


Figure 7. Process data showing sudden pressure decrease when rupture disc burst

The operators did not address the alarm when it triggered in December because they knew that work in the area would cause nuisance alarms; however, when the ECF alarm activated on January 22, 2010, operators responded. The board operator in the F3455 control room investigated and observed that the original alarm from December 21, 2009, was still displayed as the first item on the alarm screen was not acknowledged because they had become accustomed to the battery-operated transmitter causing the nuisance alarm condition.<sup>21</sup>

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<sup>21</sup> Under normal operating conditions, when an alarm point activates it will remain in an activated state until the alarm condition is cleared and acknowledged.

### 2.3.6 Second-Party Process Safety Management Audit

In 2007, an audit team of engineers and safety and health experts from other DuPont facilities conducted a 4-day second-party audit<sup>22</sup> of the Crop Protection business at Belle, which included the F3455 and SLM units. The four-member team audited the units against PSM focus areas such as MOC-subtle change, pre-startup safety reviews (PSSRs), training, process hazard analysis (PHA), mechanical integrity, and process technology. While auditing the F3455 unit and during a review of site and area management practices, the team noted the many active alarms in the unit control room: “[the] control system is not engineered to eliminate alarms from idled and secure process equipment [and as a result] the contribution to ‘nuisance’ alarms is unknown.” The audit team recommended that Belle evaluate the control system and develop an engineered solution to reduce the number of active alarms and establish a policy reflective of improvements to safely manage operations with active alarms.

During another review of SOPs and work site practices, the team noted that the Crop Protection procedure for operating with active alarms did not effectively address alarm activations from idle equipment: “The current situation can lead to human factors errors such as failing to recognize an alarm and misidentifying an alarm.” The team recommended that Belle conduct an engineering evaluation to determine changes that could separate alarms on active processes from those associated with shutdown equipment so that operators could readily identify abnormal process conditions.

Both recommendations, added to a corrective action tracking plan, were completed in fourth quarter 2008, months beyond the original target completion dates. Despite these recommendations, F3455 unit personnel continued to restart the unit while the alarm was activated, failing to recognize the impact of the burst sensor alarm.

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<sup>22</sup> A second-party audit is an independent assessment of PSM systems performed against the requirements of the DuPont corporate PSM standard.

## 2.4 Key Findings

1. The rupture disc alarm system being monitored by a battery-powered transmitter, with batteries requiring almost monthly replacement, was designated as PSM-critical<sup>23</sup> equipment by DuPont.
2. DuPont ran the equipment with an unreliable battery-powered transmitter for 18 months before executing a MOC package to convert to a wired power supply.
3. Operators expected maintenance work to trigger alarms, but planning and communication were insufficient to distinguish which alarms needed immediate attention during the turnaround and after work was completed.
4. Despite repeated incidents of rupture discs bursting, DuPont did not adequately address the cause to prevent recurrence.
5. The alarm from the transmitter did not distinguish between a condition that required immediate attention (ruptured disc burst) and a lower priority condition such as failed batteries.
6. Operators became desensitized to the rupture disc burst alarm on their computer screens.

## 2.5 Root Causes

1. DuPont's MOC process approved a design for the rupture disc alarm system that lacked sufficient reliability for minimizing the release of methyl chloride.
2. DuPont did not resolve the "nuisance alarm" condition in a timely manner despite various safety reviews.

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<sup>23</sup> PSM-critical is defined in DuPont SHE standards S21A and S24 A as components, equipment, or systems whose failure could cause, allow, or contribute to process incidents that result in death or serious injuries, significant property damage, or significant environmental impact.

## **3.0 Oleum Release (January 23, 2010)**

### **3.1 Background**

Lucite International owns the sulfuric acid recovery unit on DuPont's Belle plant property and DuPont employees operated the equipment. The SAR unit produced oleum, which is a solution of sulfur trioxide dissolved in sulfuric acid. As the sulfuric acid is consumed, the sulfur trioxide converts to sulfuric acid.

The process unit adjacent to the SAR unit used the oleum to produce methacrylic acid, an ingredient for acrylic polymers, and then returned the spent oleum to the SAR unit. The SAR unit burned off the impurities from the spent oleum and used the remaining sulfur compounds to produce clean oleum.

As a result of an unrelated, earlier inspection, the U.S. EPA ordered the Belle facility to upgrade emissions monitoring equipment or improve abatement capacity in the SAR Unit. As part of a consent decree with the U.S. EPA issued on April 24, 2009, Lucite International chose to permanently shut down the plant. The complete and final shutdown of the SAR was concluded in March 2010.

### **3.2 Incident Description**

On January 23, 2010, at about 7:40 a.m., contract personnel working near the SAR unit saw an unusual cloud in the vicinity of the oleum tower and reported a fume release to the board operator. The contractors estimated the release to be about midway along the length of a 1-inch diameter insulated pipe between the Oleum Tower Pump Tank (OTPT) and a sample station (Figure 8). The board operator asked the plant operator to go to the area of the reported leak to determine the nature of the release. The plant operator confirmed that a leak had developed on the sample piping between the OTPT and the sample station and alerted other workers in the vicinity to move to a safe area. Based on the information the plant operator

provided, at about 7:45 a.m. the board operator notified the main gate guard, who then activated a “fume alert”<sup>24</sup> to notify the facility of the release.

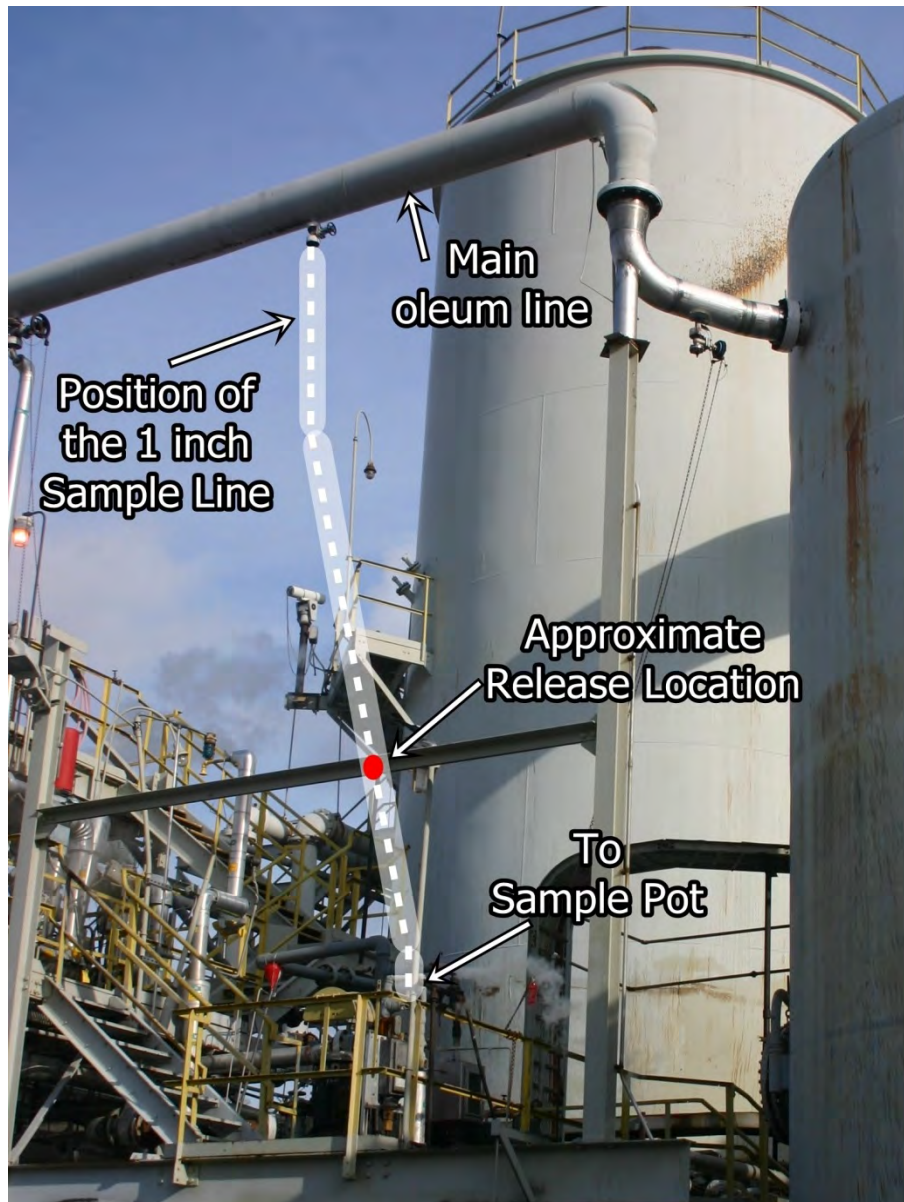


Figure 8. Photo of the position of the 1-inch sample line, which had not yet been replaced

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<sup>24</sup> Each plant in the facility has a pre-determined unique number of rings that identify it in case of a release or emergency.



A cloud of steam and sulfuric acid mist from this release is reported to have traveled in a westerly direction and dissipated in an adjacent operating unit. A concrete dike surrounding the OTPT contained liquid from the leak. There were no reports of exposure to any DuPont or contract employees or the public.

### 3.2.1 Incident Response

When the plant activates a fume alert, a klaxon bell notifies plant personnel of the location of the incident. This action also initiated a response by plant fire brigade personnel who went to the facility's fire station to obtain the plant fire engine and personal protective equipment (PPE) necessary to respond to the incident.

At about the same time the fume alert was sounded, the gate guard called Metro 9-1-1. The shift supervisor radioed the gate guard to notify the Belle Volunteer Fire Department, which then dispatched three engines to the plant. Two of the engines staged outside the plant's gate while the third went into the plant to stand by if needed.

DuPont fire brigade members arrived at the site of the release and set up a water fog spray from the DuPont fire engine and an oscillating water spray from a nearby hydrant for about an hour. After donning an acid suit and self-contained breathing apparatus (SCBA), one responder entered the area and closed a valve, which stopped the release at about 8:09 a.m. The gate guard sounded the "all clear" at about 8:27 a.m. Calculations estimate that 22 pounds of 20 percent oleum was released during the incident.<sup>25</sup>

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<sup>25</sup> 20 percent oleum has an acid content that is 20 percent greater than pure sulfuric acid.

### 3.3 Incident Analysis

#### 3.3.1 Reconstructive Analysis

CSB investigators documented the analysis of the oleum sample line to determine the incident cause, which was conducted by an independent metallurgical lab.

Caused by an unknown defect, oleum corroded through a small section of the pipe involved in the release on January 23, 2010. Starting as a pitting phenomena and finishing slightly larger than a pin hole, the corrosion penetrated the insulated stainless steel sample pipe (Figure 9).

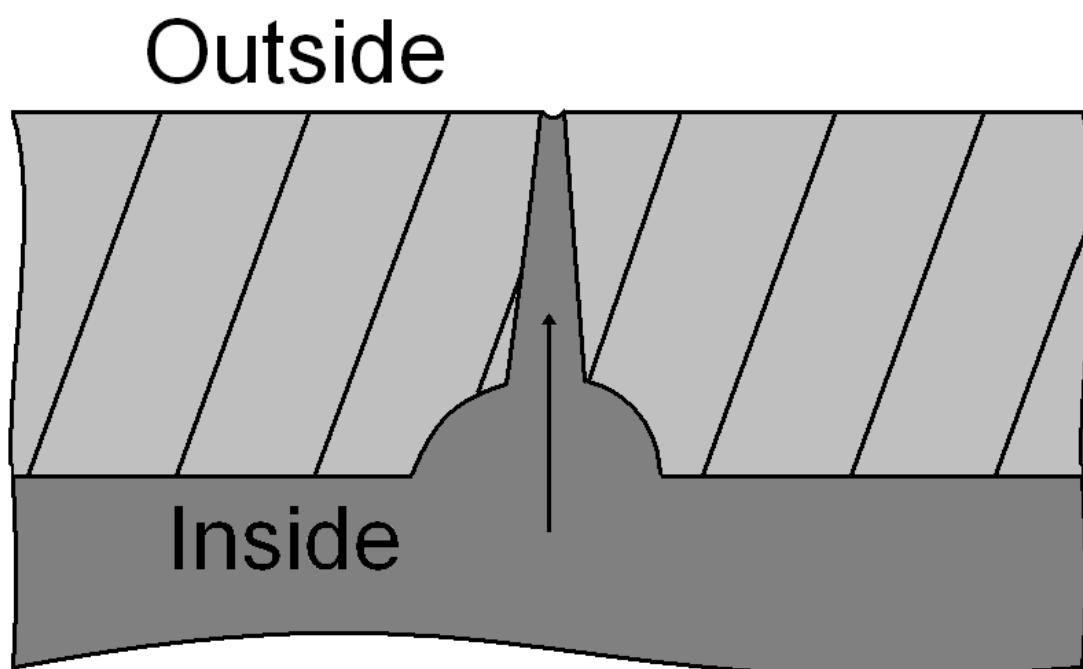


Figure 9. The pitting phenomena observed in the small initial hole of the oleum sample line wall

Once oleum was present on the exterior of the oleum pipe, it readily corroded the insulation and steam tracing line and then created a leak in the steam tracing, causing the steam and oleum to mix. This reaction created a strong solution of sulfuric acid that rapidly and effectively corroded the stainless steel sample line exterior, until a second larger hole developed at a location near the original small leak. The second hole clearly shows corrosion occurring from the outside-in (Figure 10).



Figure 10. The large hole eroded from the outside-in on the oleum sample line<sup>26</sup>

When DuPont removed the oleum-soaked insulation and cover, a large hole was visible; the acid had also corroded a large amount of the steam tracing. When the sample line was properly cleaned, inspection revealed that the smaller hole was only a few inches away from the larger hole, and after thorough examination, metallurgists concluded that the small hole in the sample line initiated the oleum release (Figure 11).

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<sup>26</sup> Due to a delay in the decontamination of the oleum pipe for purposes of evidence preservation, the size of the holes may have marginally increased from continued corrosion prior to examination.

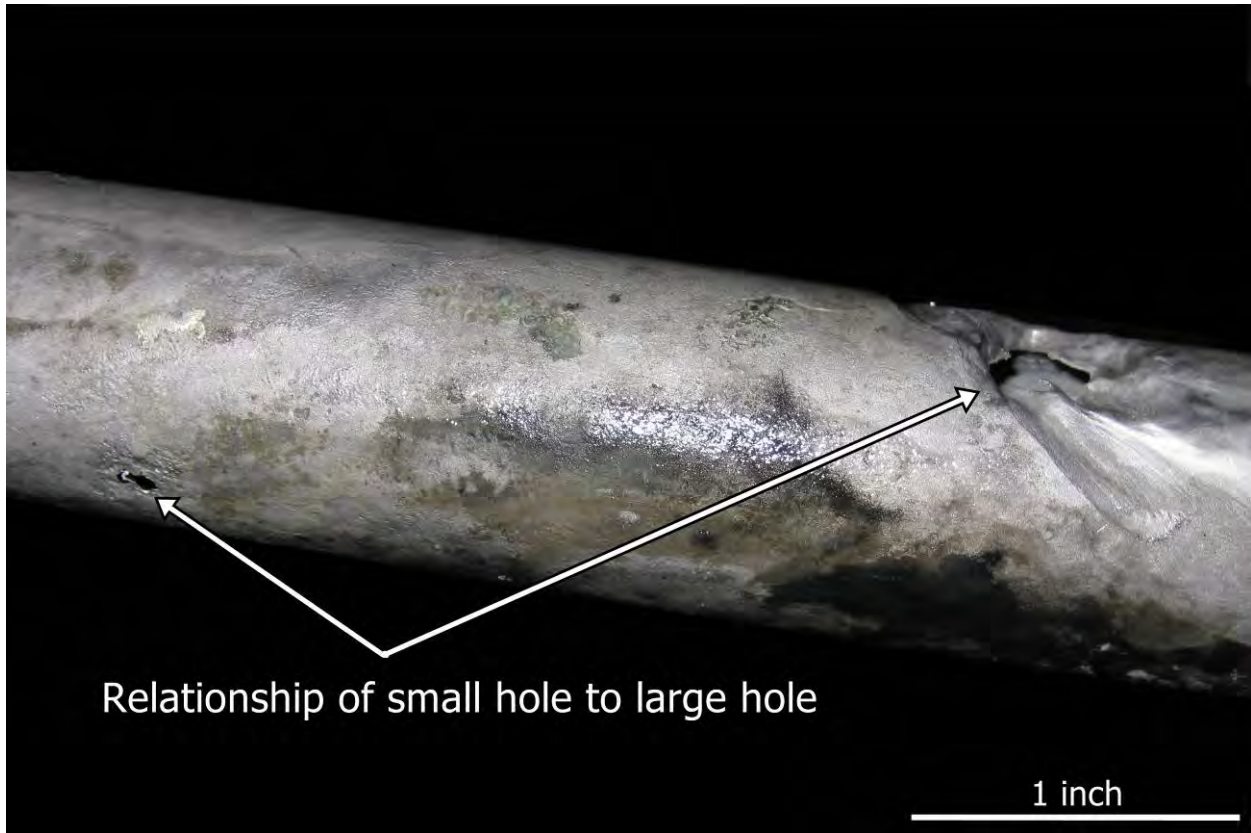


Figure 11. Photo showing the orientation of the small hole to the main hole

### 3.3.2 Pipe Testing and Analysis

The oleum sample line was tested using gamma ray radiography, ultrasonic thickness (UT), and metallographic analysis. The metallographic analysis confirmed that the sample line was fabricated from 304L stainless steel, one of the few metals approved by the DuPont Piping Standard for this oleum service.

The radiographic and UT testing showed that the pipe wall had suffered general thinning from corrosion, which is expected in most piping applications involving corrosive materials. The thinning rate can predict the service life of the pipe, and in the case of pipes routing corrosive materials, the expectation is that

roughly 1 to 2 mils<sup>27</sup> will corrode per year. UT testing and radiography revealed that general wall thinning of the sample line was much less than the predicted 1 to 2 mils per year and showed much less thinning than expected for its lifetime. This sample line had been in place for 19 years, which is not unusual for this type of service.

Only one anomaly, later deemed the initiator of this incident, was found during the testing. During visual inspection a small hole was discovered 90° off and a few inches from the large hole. Under microscopic examination, the shape of the small hole corrosion phenomenon could clearly be seen; however, its exact cause is unknown. One theory is that this small hole may have originated from some sort of manufacturing defect, but the size and shape of the pitting phenomenon suggest that if this were a manufacturing defect, the pitting would have occurred around the circumference of the pipe or along the longitudinal axis. This particular phenomenon does not fall into any easily defined defects. Due to the small size of this pitting, it is unlikely that routine non-destruction examination (NDE) techniques would have identified this defect.

### 3.3.3 Previous Incident Investigation

On January 27, 2009, almost a year to the day prior to the incident, a leak developed in the Oleum Tower circulation piping. Although the amount estimated to have been released was greater than the January 23, 2010, release (40 pounds vs. 22 pounds), supervisors deemed the situation unnecessary for an emergency shutdown and activation of a fume alert.

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<sup>27</sup> A mil is a unit of measure equal to one-thousandth of an inch (i.e., 1/1000 in).

The emergency response for the 2009 incident was inconsistent with that taken in 2010. Unlike in 2010, in 2009, a “hot line”<sup>28</sup> announcement informed plant personnel of the incident. In the incident investigation report for the 2010 incident, no mention is made of criteria that would provide guidance for the appropriate response or what distinguished the two events.

### 3.3.4 PM Program Recommendation from 2009 Incident

The internal DuPont investigation identified the following key factor in the 2009 incident:

“Pipe in acid service tends to have very localized areas of erosion/corrosion that can be easily missed while performing thickness checks. These areas are often the result of welds, the heat affected area of welds, and, disruptions or turbulence in the acid flow.”

Although DuPont realized that certain wall thinning in acid service could go undetected, one recommendation from this investigation was to incorporate all piping in oleum service into a PM schedule; however, this recommendation was not completed prior to the January 2010 incident. Moreover, the sample line involved in the January 2010 incident was not included in the PM schedule. An interview with one of the engineers responsible for arranging for this equipment to be included in the PM schedule revealed that the oversight occurred due to poor communication between DuPont and the contractors hired to perform the PM inspections.

### 3.3.5 Mechanical Integrity

The piping material, 304L stainless steel, is acceptable to carry this concentration of oleum. The expected rate of wall thinning would project the lifetime of the pipe to be approximately 40 years, and this pipe had

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<sup>28</sup> A “hot line” announcement involves notification to a pre-determined list of operating and supervisory personnel who are all informed of an incident at the facility with one call.

been in service for only 19 years. While the pipe was within the design specifications, DuPont failed to address the corrosion issues associated with acid service.

### 3.3.6 Heat Tracing Design

The oleum sample line is heat-traced<sup>29</sup> with a steam tracing line, comprised of ¼” copper tubing strapped to the outside of the sample line. The steam in the copper tracing line heats the sample line to prevent the oleum inside from freezing. Steam tracing, however, can create hot spots and often does not create even heat distribution throughout its length. A preferred method to heat piping in oleum service is electric tracing, which can be easily controlled and prevents hot spots through even heat distribution (Dillon, 1997).

As described in the Analysis Section, steam tracing played a significant role in the failure of the sample piping. Once the oleum escaped containment, the copper tracing corroded away. The oleum and steam then mixed, and the resulting extremely corrosive sulfuric acid created the larger hole. If an electric tracing line had been used, as DuPont suggests for these conditions, the large hole would not have formed, reducing the magnitude of this incident.

## 3.4 Key Findings

1. An internal DuPont investigation report from a prior oleum leak recommended including all piping in a PM thickness monitoring program. The CSB found no evidence that the piping in the January 23, 2010, incident was included in the program.
2. The general wall thinning rate estimate for the oleum service was conservative. However, highly localized corrosion attack cannot be predicted by this method.

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<sup>29</sup> The protection of a liquid-filled pipe against freezing by installing heat tubing or heating cable around or along the pipe

### 3.5 Root Causes

1. Corrosion caused a small leak in the oleum pipe under the insulation.

## 4.0 Phosgene Release (January 23, 2010)

### 4.1 Background

#### 4.1.1 Phosgene

Phosgene, in liquid and gaseous forms, is colorless and highly toxic and has a characteristic odor of freshly cut hay or grass, with a boiling point of 8° C (47° F), and is liquid in cold weather, gas in warmer weather. At room temperature phosgene is a dense gas that is heavier than air. Phosgene is manufactured through the reaction of carbon monoxide and chlorine and is used widely in industry as a chemical intermediate for isocyanate-based insecticides, polymers, and pharmaceuticals.

Inhalation is the primary route of exposure to phosgene. The OSHA 8-hour TWA PEL for phosgene is 0.1 ppm<sup>30</sup>; the NIOSH IDLH concentration is 2 ppm. The odor threshold<sup>31</sup> ranges between 0.4 and 1.0 ppm, which is higher than the OSHA PEL; therefore, odor is not a reliable detection method for phosgene, as injury may occur before the odor becomes prominent. Phosgene gas may irritate skin and eyes upon contact at lower concentrations. Liquid phosgene contact with skin can also cause severe chemical burns at higher doses.

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<sup>30</sup> The NIOSH- and ACGIH-recommended TWA concentrations are also 0.1 ppm for phosgene.

<sup>31</sup> An odor threshold is the lowest airborne concentration that can be detected by a population of individuals. The range of detection varies among individuals.



Phosgene inhalation can result in two mechanisms of injury to the respiratory tract, both of which can result in pulmonary edema<sup>32</sup> at high concentrations. Inhaled phosgene slowly undergoes hydrolysis and forms HCl, which results in upper respiratory irritation and burning sensations, cough, and chest oppressions. Symptoms may not appear until several hours after exposure. Phosgene also reacts with proteins in the pulmonary bronchioles and alveoli, disrupting the blood-air barrier in the lungs and resulting in increased lung fluid. Pulmonary edema can be present in victims as long as 40 hours after exposure and may last days depending on the concentration and duration of the exposure.

#### 4.1.2 Phosgene Stainless Steel Hose Transfer Operation

The Small Lots Manufacturing Unit (SLM) runs on a campaign<sup>33</sup> basis and is divided into two processes: the “front end” and “back end.” The front end process makes five isocyanate intermediate products.

Phosgene used to produce the five intermediate products is fed to a process from 1-ton cylinders stored in the phosgene shed at the SLM unit. The phosgene cylinder storage shed is a covered, partially walled structure where the phosgene transfer and storage operations occur (Figure 12). All equipment used for these purposes is in or around the shed. The shed contains no mechanical ventilation or exhaust systems to control phosgene leaks, only natural ventilation flowing through the shed wall opening from the atmosphere.

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<sup>32</sup> Pulmonary edema, which occurs when fluid accumulates in the lungs, leads to impaired gas exchange and may cause respiratory failure. It is due to either failure of the heart to remove fluid from the lung circulation (“cardiogenic pulmonary edema”) or direct injury to the lung parenchyma (“noncardiogenic pulmonary edema”).

<sup>33</sup> The front end of the SLM unit manufactures several types of isocyanate intermediates on a demand-based schedule.

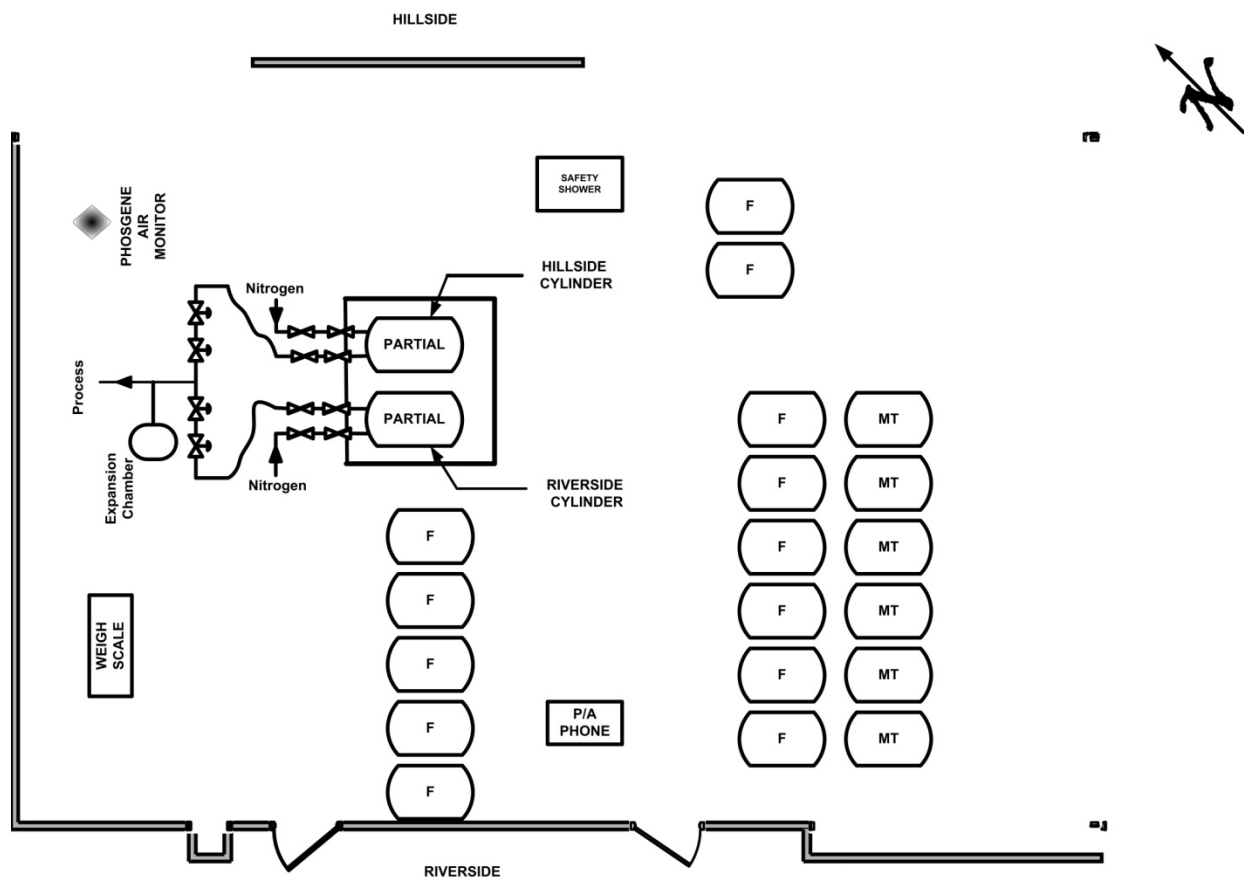


Figure 12. Phosgene shed and full (F) and empty (MT) cylinder locations on day of incident (not to scale)

During normal operation, two cylinders are staged on weigh scales and each is connected to the process with two, 0.25-inch diameter by 48-inch long PTFE-lined, 304 stainless steel overbraid hoses. One hose transfers liquid phosgene to a steam vaporizer and one provides 70-psig nitrogen to the cylinder. The scales record the weight of the in-service cylinder and when the container is nearly empty, an alarm notifies the board operator, who then directs the plant operators to switch to a full cylinder. This switch is completed by opening valves to the full cylinder and closing valves to the empty cylinder. The hoses remain coupled in this operation and plant SOPs do not require enhanced PPE such as a fully encapsulated suit and breathing air. Under normal operating conditions, the process consumes two to three cylinders of phosgene per day.

The SOPs do require operators to don a fully-encapsulated suit with supplied breathing air when they replace an empty cylinder with a full cylinder. After clearing all phosgene from the stainless steel hose with a nitrogen purge under vacuum to a scrubber, the hose is isolated from the vent piping and disconnected from the empty cylinder. Operators then replace the empty cylinder on the scale with a full cylinder and connect the stainless steel hose back to the new cylinder.

Maintenance mechanics replace stainless steel hoses in phosgene service when a work order is generated to change out the hoses. The DuPont SOPs for the change-out frequency of the nitrogen and phosgene hoses directs replacement every 30 days.<sup>34</sup>

Hose assemblies are fabricated by a number of manufacturers to DuPont's specifications for phosgene and nitrogen hoses and arrive pre-assembled. The hoses are stored in plastic bags in the maintenance shop. Prior to connecting the hoses to the phosgene cylinders, the maintenance mechanics install valves on either end of the hose. Hoses removed from service are decontaminated in a water bath and then disposed.

#### 4.1.2.1 VanDeMark Chemical, Inc.

VanDeMark Chemical supplies phosgene to the Belle plant in 1-ton cylinders. VanDeMark, located in Lockport, NY, is the only North American company that both produces and distributes phosgene. They distribute phosgene and phosgene derivatives in 1-ton cylinders. Each VanDeMark cylinder is 87 percent full and contains 2,000 pounds of phosgene. Each U.S. Department of Transportation-regulated cylinder has two valves with a seal plug screwed in the outlet covered by a flanged and gasketed bonnet to protect the valves and prevent leaks during transport. The Belle plant receives phosgene cylinders via truck and

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<sup>34</sup> DuPont's former maintenance management process directed that hoses be changed every 2 months.

they are unloaded at the phosgene shed; empty cylinders are loaded onto the truck and returned to VanDeMark.

#### 4.1.2.2 Use of Personal Protective Equipment (PPE)

DuPont safety procedures include two levels of PPE required for work in the phosgene cylinder shed on the SLM unit, based on the connection status of the phosgene cylinders. When the phosgene cylinders are connected to the process and no breaks in the phosgene lines are occurring, the standard required PPE for the SLM unit is a hard hat, steel-toed safety shoes, safety glasses, flame resistant clothing (FRC), and a phosgene indicator badge. Work with this level of protection includes

- entering the phosgene shed to check cylinder scale weights,
- opening and closing valves to switch from one cylinder to another, and
- operating the crane when loading and unloading full or empty cylinders in the phosgene shed

The Belle Plant SOPs for disconnecting a phosgene cylinder require operators to wear a chemical suit (gloves, boots, and hood) with supplied breathing air in addition to the PPE listed above while performing the work. During all phosgene cylinder line break operations, another operator, wearing standard PPE, stands outside the shed to monitor the breathing air supply of the operator performing the work.

At the time of the incident, the employee fatally exposed to phosgene was wearing the standard PPE. This met DuPont operating standards for the task he was performing, because he was likely checking cylinder weights in preparation for switching to the partially filled riverside cylinder. The Belle Plant PPE requirements and SLM unit procedures did not require him to don a chemical suit, with supplied air, during this activity.

#### 4.1.2.3 Phosgene Indicator Badge

Belle Plant safety procedures require all personnel (operators, contractors, managers) and visitors in the SLM unit to sign a log sheet and obtain a phosgene indicator badge from the SLM control room prior to entry and to wear a phosgene indicator badge in their breathing zone (Figure 13). Phosgene indicator

badges change color when exposed to phosgene and the color indicates the concentration 1 minute after exposure. After 2 consecutive days of use, personnel using badges must discard and replace their indicator badge to ensure accurate sensitivity.<sup>35</sup>

Two types of phosgene indicator badges are available for use in the SLM unit. For work tasks not involving supplied air, personnel clip SafeAir<sup>®</sup> System phosgene badges (Morphix Technologies) to the collar or pocket of FRC near the breathing zone. The badges change from white to pink or red to indicate dose, concentration, or duration of exposure. In addition to badges, the SafeAir system uses a color comparator wheel to detect exposure dose and the presence of phosgene between 0.9 and 100 ppm-min.<sup>36</sup>

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<sup>35</sup> The manufacturing specifications state that the maximum recommended sampling time for each badge is 3 days. The Belle plant requires phosgene badges to be replaced after 2 days to ensure accurate detection and avoid discoloration or interference with other chemicals.

<sup>36</sup> Parts per million-minute (ppm-min) is the concentration of a contaminant in air related to the exposure time through inhalation; 48 ppm-min = 480 minutes of exposure at 0.1 ppm concentration.

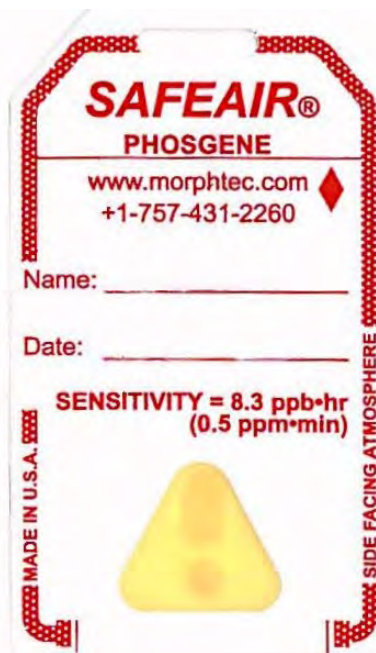


Figure 13. SafeAir Phosgene Dosimeter Badge<sup>37</sup>

For work tasks in the SLM unit requiring supplied air, all personnel must wear a CheckAir<sup>®</sup> phosgene badge inside the mask of their supplied air respirator. The CheckAir detector (Morphix Technologies) detects exposure dose concentrations between 0.9 and 100 ppm-min. The color comparator wheel for detecting exposure concentrations of the CheckAir detectors differs from that of the SafeAir badges.

#### 4.1.2.4 Alarms

The SLM unit has 12 phosgene sensors placed in and around it to continuously sample and record phosgene concentrations every 30 seconds; concentrations of phosgene are detected via an electrochemical diffusion sensor within a range of 0.05 to 1 ppm. One phosgene sensor is located in the phosgene shed, six are in the SLM building, and two are located outside the building. Three sensors are

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<sup>37</sup> The badge in Figure12 has a range of 0.5 to 450 ppm-min. The SafeAir badge worn by the exposed employee had a range of 0.9 to 100 ppm-min.

on the fence line of the facility along the Kanawha River, approximately 120 feet from the phosgene storage shed.

The analyzer readings are monitored by the DCS in the SLM control room, and concentrations in excess of 0.05 set off audible and visual alarms at the board operator's work stations. Concentrations equal to or greater than 0.05 ppm set off a medium-high alarm and concentrations at or above 0.1 ppm set off a high-high alarm. The CSB could find no evidence that audible or visual alarms were in service in the phosgene shed when the release occurred.

On the day of the incident, the phosgene release activated alarms in the control room for 4 of the 12 analyzers in and around the SLM unit. The phosgene analyzer in the shed recorded concentrations ranging from 0.04 to 1.0 ppm for approximately 50 minutes following the initial release. Two of the three fence line monitors triggered alarms, with the maximum recorded concentration of 0.27 ppm on a monitor located approximately 120 feet from the phosgene shed along the river. Another monitor, located on a spill tank outside the SLM unit building, also recorded a concentration of 0.04 around the time of the release.

All 12 phosgene analyzers chosen by DuPont have a maximum detectable concentration of 1 ppm. The analyzers do not record actual values for concentrations in excess of 1 ppm; therefore, if phosgene concentrations exceeded the detection range at the analyzer sample point, the values were only recorded as 1 ppm.

#### 4.1.3 Phosgene Highly Toxic Material Guardian Committee

DuPont's Phosgene Highly Toxic Material Guardian Committee focuses on the safe management of phosgene at applicable DuPont facilities. DuPont has several guardian committees for HTMs used within the company. Representatives, known as phosgene guardians, from all DuPont sites that produce or consume phosgene comprise the committee. Managers from affected processes, corporate health and safety representatives, engineers, and industrial hygiene specialists also participate. The Phosgene

Guardian Committee holds meetings twice a year to share learnings and discuss phosgene handling issues.

DuPont has an HTM manual for phosgene, a company protocol that includes requirements and guidelines for the safe design and operation of processes that generate or use phosgene. The primary purpose of the manual is to reduce the likelihood that phosgene could harm employees or the public. The requirements of the manual are mandatory for all DuPont facilities with enough phosgene to impose a significant offsite hazard as determined by a chemical consequence analysis of offsite exposure. Members of the Phosgene Committee conduct a second-party audit every 3 years of all facilities using phosgene against the requirements and guidelines set forth in the phosgene HTM manual. The Phosgene HTM Committee audited the SLM unit at the Belle Plant in September 2006; the next audit was scheduled for January 25, 2010, just two days after the phosgene release incident.

## 4.2 Incident Description

The third incident occurred on January 23, 2010, between 1:45 and 2:00 p.m. in the SLM unit, when the stainless steel braided transfer hose connected to a partially filled, but not in service, 1-ton phosgene cylinder failed catastrophically. This incident occurred in the phosgene shed. When the release occurred, an operator was in the phosgene shed inspecting the status of the hillside<sup>38</sup> phosgene cylinder as he anticipated the cylinder was nearly empty and would need to be switched. He was sprayed across the chest and face with liquid phosgene remaining in the riverside hose from a previous transfer operation.

DuPont estimates that about 2 pounds of phosgene were released to the atmosphere when the hose failed. The CSB concurs with this estimate, and further calculated that the operator would have received a lethal dose of phosgene in less than a tenth of a second (Appendix D).

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<sup>38</sup> The cylinders are commonly referred to as the “hillside” or “riverside” cylinders based on their orientation in the phosgene shed relative to the hills north of the building and the Kanawha River to the south.



Immediately after the operator was sprayed, he called for assistance on the SLM unit public address phone in the phosgene shed. A co-worker who responded to the call for assistance noticed the victim's phosgene dosimeter badge (Figure 13) was discolored, indicating an exposure. The co-worker directed the exposed worker to a plant truck to transport him to the plant's medical center for assessment and treatment. As they drove to the medical center, the two workers were met by the Shift Supervisor and the exposed worker was transferred to the shift supervisor's vehicle to complete the trip. While en route to the plant's medical center, the front gate guard was radioed and advised to call Metro 9-1-1 and request that an ambulance respond for a medical emergency. The exposed worker, while at the medical center waiting for the ambulance, chose to wash his face and hands, but there is no evidence or record that he was placed in a safety shower to wash off, as instructed by the emergency procedures, or that any decontamination activity took place beyond his washing his face and hands. He was given a change of coveralls to put on in exchange for the work clothes he was wearing at the time of exposure. The gate guard called Metro 9-1-1 at 1:59 p.m., requesting transport for a medical emergency patient to the hospital. The 9-1-1 dispatcher asked if there was a chemical release; however, the gate guard, who was unaware of the situation, responded that there was no release and that the response was for a medical emergency. As part of the Metro 9-1-1 emergency response protocol, the dispatcher asks for specific information to ensure that responders are as informed as possible prior to arrival at the scene. At 2:03 p.m., an ambulance was dispatched from the Kanawha County Emergency Ambulance Authority (KCEAA).

At 2:08 p.m., responding EMTs asked Metro dispatchers if more information was available about the victim. When Metro called DuPont to get more information, the line was busy. EMTs also wanted to know if there was a chemical exposure, but Metro 9-1-1 could not get that information from DuPont. Six minutes later, the EMTs arrived at the DuPont gates.

EMTs were directed to the DuPont medical center to meet the exposed worker. As the EMTs gathered the worker for transport, they were given a written phosgene treatment protocol intended to be used at the

hospital to provide treatment. While the worker was being transferred to their care, DuPont employees told the EMTs that the victim had been exposed to liquid phosgene.

The EMTs left the facility with the victim at 2:26 p.m., or 27 minutes after the first call to Metro 9-1-1. During transit and after arrival at the hospital at 2:34 p.m., the victim was lucid, conscious, and talking clearly to the emergency responders and attending physician. Until the attending ER physician consulted the company-provided phosgene treatment protocol, which advised 48-hour monitoring for suspected phosgene exposures, he considered sending the victim home based on his condition shortly after arriving at the hospital. A baseline X-ray revealed no congestion in the victim's lungs. At about 5:30 p.m., or almost 4 hours after exposure, the operator's condition began to rapidly deteriorate. Over the next 29 hours, the victim received treatment from a variety of physicians, but his condition failed to improve and he died at 9:27 p.m. on Sunday, January 24, 2010.

Post-incident, KCEAA staff voiced concerns regarding the quality and timeliness of information DuPont provided to Metro 9-1-1 dispatchers and responding EMTs. The concerns raised address the need to ensure that emergency responders and their equipment are not exposed to contaminants and that the victims they are assisting receive optimum care in transit for medical treatment. A review of comparable responses by KCEAA EMTs in the region revealed that the response time to DuPont and from there to the hospital was not unduly delayed by the lack of information. A sampling of similar emergency responses reveal an average response time from the initial call to Metro 9-1-1 until arrival at the hospital to be about 36 minutes. Total elapsed time for the response time on the day of the exposure was 35 minutes.

Although the emergency response and transport of the victim was not delayed during this incident or the oleum release, because of a lack of clear, accurate information regarding the material involved, response procedures have since been modified by the administrators of Metro 9-1-1. These modifications mandate that EMS units will not report directly to the site of an incident until clear information has been provided such that EMS personnel will not be at risk of unknown contaminants/threats. This change in response

protocol was incorporated after several incidents in the Kanawha Valley. The CSB considers the change in response protocol significant enough to define the cause and effect of the communication gap as a near miss. Several key factors that contributed to poor communication, included the absence of a process knowledgeable person who was assigned to convey information to the dispatchers, and the lack of a direct line to the Metro 9-1-1 emergency operations center, must be recognized and addressed.

One confirmed and one possible phosgene exposure to workers occurred after the initial release. The first occurred when a co-worker responded to the call for assistance immediately after the phosgene hose ruptured. As he drove the victim to the facility's medical building, the co-worker's dosimeter badge became slightly discolored, indicating a phosgene exposure.

A possible source of this exposure was phosgene vapor in the atmosphere as recorded on one of three fence line monitors about 120 feet from the shed along the river. Another possible source was from the victim's clothing, which may have been saturated with phosgene immediately after the release. When interviewed, this employee indicated that he was subjected to pulmonary function tests afterward and reported no signs of adverse effects.

A second possible exposure occurred when an employee working in the SLM unit went toward the phosgene shed shortly after the release. He reported in an interview that as he got closer, he noticed a smell that he had not encountered before or since. He recalled that the odor was not strong or offensive as would be expected with ammonia or chlorine, but noticeably different from any odors he had smelled in the past. Being unfamiliar with the characteristic, fresh mown hay odor associated with phosgene he left the area.

Although the phosgene shed area has flashing lights to alert against entry into the area during cylinder changes, there is no evidence that a fume, medical, or plant radio alert sounded at any time during this release episode to warn operators and maintenance personnel to avoid coming near the phosgene shed.

#### 4.2.1 Community Impact

Two of the three fence line analyzers recorded a maximum concentration of 0.15 and 0.27 ppm<sup>39</sup>

phosgene, indicating that phosgene concentrations had traveled offsite toward the Kanawha River.

However, no member of the public reported phosgene exposure symptoms the day of the incident nor did the U.S. Coast Guard restrict river traffic or conduct air monitoring as it had a day prior as a result of the methyl chloride release.

### 4.3 Incident Analysis

#### 4.3.1 Hose Failure Analysis

Post-incident inspections of the stainless steel hoses used for the two phosgene cylinders connected to the process identified comparable degradation patterns. Their failure was associated with corrosion that developed in approximately the same location on hoses used to transfer phosgene from the riverside and hillside cylinders.

Investigators found that while the majority of tags attached to the hoses to indicate the intended service were secured in place with plastic ties and metal clamps—as was normal—one manufacturer's tag was secured with clear plastic adhesive tape (this tag applied by the manufacturer also provided identification information). The corrosion identified on the two hoses associated with the hillside and riverside cylinders was localized under the area covered by the clear plastic adhesive tape securing the tag.<sup>40</sup> The characteristics of the transfer hose, consisting of a core constructed of permeable PTFE and braided 304-

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<sup>39</sup> ERPG-2 value for phosgene is 0.20 ppm and at this concentration “all could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action” (AIHA, 2008).

<sup>40</sup> Witnesses could not provide an exact date that the hoses came into the facility with the tags affixed with adhesive tape.

stainless steel, provided a suitable environment under the adhesive tape for stress corrosion cracking (SCC) to occur.

In order to provide comparative data, hoses from the hillside, riverside, and exemplars of similar age and new assembly were sent to an analytical lab for testing and analysis. The tests established that all of the hoses were constructed with 304-stainless steel and the construction material for the inner core of the hoses was PTFE, as expected.

#### 4.3.2 Effect of Plastic Adhesive Tape

The PTFE, 304 stainless steel, and the clear plastic adhesive tape contributed to the incident. The PTFE inner core was permeable and susceptible to phosgene vapor diffusing through the hose. The adhesive tape used to secure the tag contributed to the retention of phosgene gas on the exterior of the stainless steel overbraid. The phosgene gas converted to HCl, and 304 stainless steel overbraid is subject to corrosive attack by HCl. Since the clear plastic adhesive tag trapped the phosgene permeating through the PTFE inner core, the resulting concentration of HCl was much higher under the tag than elsewhere on the hose (Figure 14).

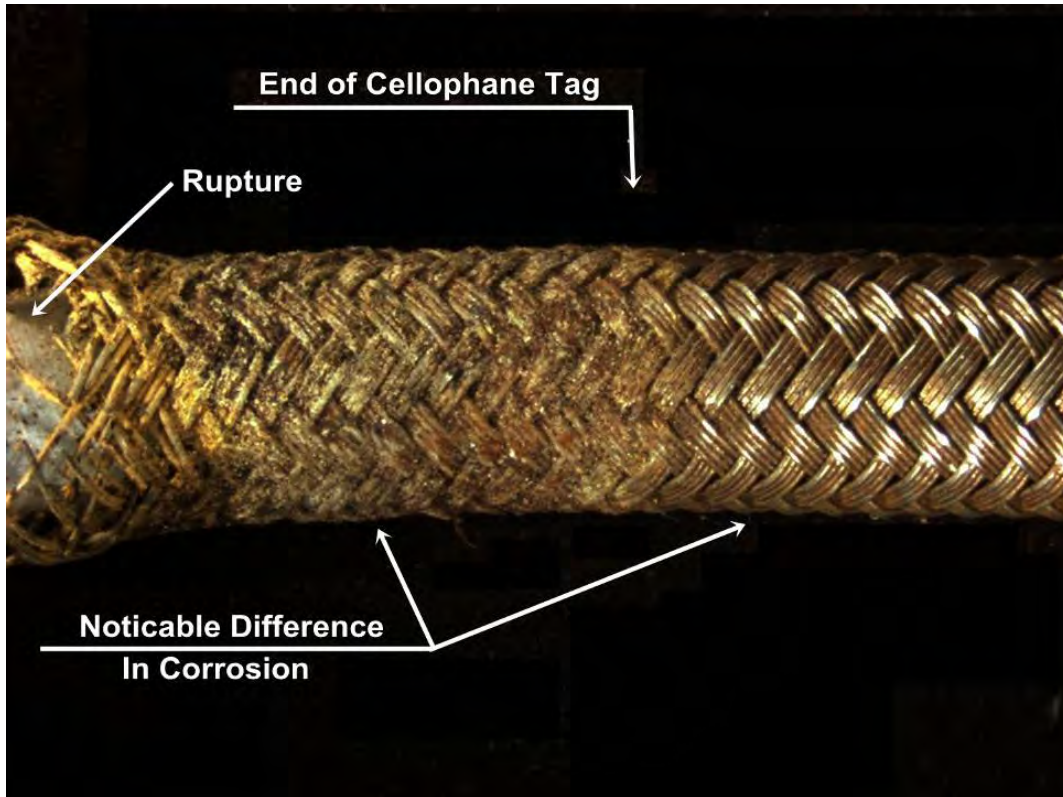


Figure 14. The distinct effect of the clear plastic adhesive tag on the corrosion of the stainless steel overbraid

Additionally, at the time of the incident, the isolation valves on the phosgene hose on the riverside cylinder were closed, which retained liquid phosgene in the hose and pipe between the valves that isolated the cylinder from the process. The heavy corrosion of the stainless steel over braid coupled with the length of time the hose had been in service and thermal expansion of the isolated liquid phosgene, caused the hose to fail catastrophically. When this failure occurred, the worker was exposed as he walked nearby to check on the status of the adjacent, in-service cylinder.

#### 4.3.3 Hose Degradation Issues

Although the maintenance plan for the hillside and riverside hoses prescribed a regular change-out schedule of 30 days for the hoses, work orders show that change-out frequency was neither systematic nor

predictable. At least three times from 2006 to 2010, phosgene hoses were left in service from four to seven months without being replaced.

#### 4.3.4 Hose Change-out Frequency

Several times each year, the phosgene process is halted so the plant can produce a material requiring the physical removal of phosgene, including all full or empty 1-ton cylinders, from the phosgene shed. Table 2 shows the change-out frequency of the phosgene hoses in the SLM unit and the periods when SLM did not run processes using phosgene. The most recent recorded instance where phosgene was not used in the process was between September and November 2009, 2 months prior to the incident. Work orders for changing out the phosgene hoses indicate that the stainless steel transfer hoses connected at the time of the incident had been in service for more than six months. This included a removal of the phosgene system change out in September 2009 when the hoses could have been changed out.

<b>Hose Change-out Frequency</b>		
Month/Year	Phosgene Hoses	Phosgene Used
Jul-05	Changed	Phosgene Used
Aug-05	Changed	
Sep-05	Changed	
Oct-05	Changed	
Nov-05	Changed	
Dec-05		
Jan-06		Phosgene Used
Feb-06		Phosgene Used
Mar-06	Changed	Phosgene Used
Apr-06		Phosgene Used
May-06		Phosgene Used
Jun-06	Changed	Phosgene Used
Jul-06	Changed	Phosgene Used
Aug-06		
Sep-06		
Oct-06	Changed	
Nov-06	Changed	
Dec-06		
Jan-07		Phosgene Used
Feb-07		Phosgene Used
Mar-07	Changed	Phosgene Used
Apr-07		Phosgene Used
May-07	Changed	Phosgene Used
Jun-07		Phosgene Used
Jul-07		Phosgene Used
Aug-07		
Sep-07	Changed	
Oct-07		
Nov-07		
Dec-07		
Jan-08		Phosgene Used
Feb-08		Phosgene Used
Mar-08		Phosgene Used
Apr-08	Changed	Phosgene Used
May-08	Changed	Phosgene Used
Jun-08		Phosgene Used
Jul-08	Changed	Phosgene Used
Aug-08	Changed	
Sep-08		
Oct-08		
Nov-08		
Dec-08		
Jan-09	Changed	Phosgene Used
Feb-09		Phosgene Used
Mar-09		Phosgene Used
Apr-09		Phosgene Used
May-09		Phosgene Used
Jun-09	Changed	Phosgene Used
Jul-09		Phosgene Used
Aug-09		
Sep-09		
Oct-09		
Nov-09		
Dec-09		
Jan-10		Phosgene Used

Table 2. Phosgene hose change-out frequency



The CSB found that change-out frequency was intended to be governed automatically by the Belle facility's SAP maintenance program. Some supervisors also relied on the maintenance coordinator remembering to initiate the change-out.

#### 4.3.5 SAP Work Process

DuPont uses the plant maintenance module of SAP enterprise resource planning software<sup>41</sup> to schedule the change-out of phosgene hoses at pre-determined 30 day intervals. The SAP system is programmed to issue the work orders for hose replacement to prevent the release of phosgene; thus, maintaining accurate data in the SAP database is crucial to protect against phosgene exposure.

In late 2006, SAP data managing the change-out frequency of the phosgene hoses at the Belle facility were changed; consequently, SAP stopped automatically issuing work orders to change the hoses, but plant personnel were unaware that SAP no longer automatically issued the work orders. The CSB requested additional information regarding the change however; DuPont could not determine who changed the SAP data, why it was changed, or when the change was executed. No back-up layer of protection ensured that the hoses were changed at the pre-determined frequency, such as a weekly critical equipment maintenance check-sheet or an inspection tag. With SAP no longer automatically issuing work orders to change the hoses, the system did not trigger maintenance notifications to change out the hoses at assigned intervals.

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<sup>41</sup> Enterprise resource planning software is a type of database software that allows data related to flows of money and other resources in areas such as accounting, supply chain management, sales and marketing, manufacturing, maintenance, and project management to be recorded and accessed.

#### 4.3.6 Near-Miss Phosgene Incident

On the morning of the phosgene incident, operators asked maintenance personnel to replace the phosgene hose on the hillside cylinder because of a suspected flow restriction. Although the cylinder was still about half full, it was removed from service and replaced with the full riverside cylinder.

The hillside phosgene supply hose and valve assembly were removed and decontaminated in a water bath. When the hose was removed from the water, the clear adhesive ID tag had fallen off, revealing a broken stainless steel braid and collapsed PTFE liner, a possible cause of the flow restriction (Figure 15).



Figure 15. Damaged hillside phosgene hose removed from phosgene cylinder. The plastic adhesive tag that covered the damaged section fell off during the hose decontamination procedure.

An operator stated during an interview that when he saw the physically defective section of the frayed hose, he told his co-workers, stressing that the hose was close to rupturing and that they were lucky to have found it and changed out the hose in time. Unfortunately, this discovery was not captured as a near-miss, since supervisors were not made aware of the issue.

Operators told the CSB investigators that they had never seen a phosgene stainless steel hose braid corroded to the point of separation. Although they were surprised and concerned about their finding, they decided, since supervisory staff does not work on weekends, to wait to tell the supervisors about the discovery on Monday morning, about 48 hours later. Operators said that they expected that the supervisors would conduct a full investigation; however, since the incident occurred on a Saturday, it was not investigated. Had there been a system in place for operators to report near-miss incidents on weekends to supervisory staff, the near-miss investigation may have been properly initiated prior to the fatal release.

#### 4.3.7 Mechanical Integrity

The DuPont P3H Standard lists acceptable construction materials for flexible hoses used in HTM service and recommends three different hoses acceptable for use with phosgene: H2, H7, and H9 (Table 3).

DuPont P3H Standard Hoses for Phosgene Service		
Name	Specifications	
<b>H2</b>	Inner core material:	Monel® 400, corrugated
	Reinforcement material:	Monel® 400 overbraid
	End fitting material:	Monel® 400 SCH. 80
	Core/fitting connection method:	Welded, full penetration
<b>H7</b>	Inner core material:	Hastelloy® C276, corrugated
	Reinforcement material:	Monel® 400 or Hastelloy® C276 overbraid
	End fitting material:	Hastelloy® C276 stub ends
	Core/fitting connection method:	Welded, full penetration
<b>H9</b>	Inner core material:	Teflon <sup>42</sup> PTFE, helical, corrugated, taped or extruded construction, unpigmented or conductive
	Reinforcement material:	PVDF (Kynar®) double overbraid
	End fitting material:	Monel® 400, Hastelloy® C276, or Teflon® encapsulated SS
	Core/fitting connection method:	Crimped (or swaged)

Table 3. Flexible hoses for phosgene service as listed in the DuPont P3H Standard: Flexible Chemical Hose for Highly Toxic Services

The Belle facility did not use any of the P3H specified hoses and configurations. Instead, the facility used a flexible hose made of a Teflon® PTFE inner core and a braided stainless steel reinforcement material; even though stainless steel is not recommended for phosgene service as it is susceptible to SCC from chlorides. Phosgene, which can readily react with air to produce chlorides, can permeate PTFE, directly exposing the stainless steel braid to chloride attack.

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<sup>42</sup> Teflon is the DuPont-registered trademark for PTFE.

#### 4.3.8 Flex Hose Materials of Construction

The Belle facility deferred to corporate experts and the La Porte<sup>43</sup> facility, where flexible hoses were being used for phosgene service.

The discussions about flexible hoses began in 1987, when corporate experts suggested the use of Monel metal for both the hose core and hose overbraid, since it resists chloride SCC. However, the La Porte plant asserted that its history with Monel metal was less than desirable; one correspondent noted, “The La Porte plant was considering testing Kynar-overbraid<sup>44</sup> covered Teflon hose because of discoloration and gradual deterioration of the Monel.”

An expert from DuPont corporate told Belle that the discoloration was not a problem:

Reports from La Porte that Monel braided hoses were corroding in phosgene service are not exactly true. The hoses at that time were Teflon lined, with a Monel outer overbraid. Due to permeation of phosgene through Teflon, the Monel was slightly attacked, forming a green surface film known as a ‘patina’<sup>45</sup> which is common to all copper-based alloys.

A Belle representative sent a questionnaire to La Porte in August 1987 to evaluate its hose program. The questionnaire revealed that La Porte had been using PTFE-lined stainless steel hoses for the previous 3 to 4 years and that they were replaced every 3 months. It reported that the majority of the hose failures were due to fatigue, and that the facility was using stainless steel because it is not as susceptible to failure from

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<sup>43</sup> DuPont uses phosgene at five of its facilities, including the one in La Porte, TX.

<sup>44</sup> The Kynar hose was also not pursued due to pre-conceived flexibility limitations.

<sup>45</sup> Patina is a green film formed naturally on the surface of copper and copper-based metals, and can most easily be observed on old pennies.

fatigue and bending stresses as are Monel and Kynar hoses. After reading the questionnaire, the corporate DuPont expert wrote,

I still believe that Monel is the best choice for material of construction for phosgene unloading hoses (and definitely for the fittings). I am surprised that La Porte is using Teflon-lined hose with stainless overbraid since Teflon is known to be permeable and the phosgene is known to attack the stainless.

The DuPont expert further stated,

Admittedly, the Monel hose will cost more than its stainless counterpart. However, with proper construction, and design so that stresses are minimized...useful life should be much greater than 3 months. Costs will be less in the long run and safety will also be improved.

Correspondence or other records that would explain why the expert's recommendation went unheeded at La Porte and why the Belle staff decided to follow the La Porte approach was not discovered during the investigation. However, Belle decided to follow La Porte's example, and adopted a hose design not recommended by their P3H Standard or by a DuPont corporate expert.

The phosgene hose replacement frequency at Belle is defined in DuPont's Phosgene Hose Assembly Procedure: "Due to the extremely hazardous nature of phosgene the hose assemblies are replaced every 2 months."

However, the PM schedule in SAP is actually set to a replacement frequency of 30 days and this procedure does not effectively communicate to operators why these hoses must be replaced so frequently. If left on too long, the accepted corrosion condition poses a serious risk to the facility and the community.



Figure 16. Flex hose comparison photographs: (top to bottom) ruptured riverside hose, flow restricted hillside hose, a new hose with attached ID tag

#### 4.3.8 Non-routine Job Planning

Operators told the CSB investigators about the difficulty in maintaining the required flow of phosgene from one of the two cylinders on the weigh scales the day prior to the exposure incident. The phosgene flow from the cylinder to the process was inadequate; thus, they performed a non-routine operation to establish a steady flow of phosgene because they suspected a plugged hose or a malfunctioning automatic feed control valve.

To minimize disruption of the phosgene flow to the process, operators switched to the riverside cylinder, which operated as expected and supplied the normal flow rate. Continuing throughout the day and into the next, operators repeated switching to the riverside cylinder as the flow from the hillside cylinder became low enough to begin to affect the process. When valves for each of the respective transfer hoses were closed, liquid phosgene was not evacuated as stated in the SOP for switching from one cylinder to

another. Since the operators were not fully aware of the hazards of thermal expansion, liquid phosgene remained in the hoses as the cylinders were switched.

The CSB investigators reviewed DCS flow and weight data and observed a distinct difference in the ability of the riverside cylinder to provide the needed flow rate of phosgene compared to the hillside cylinder in this operation. All of the DCS information the operators received as a result of the non-routine cylinder switching indicated that their actions were successfully maintaining the smooth operation of the unit.

The operators, however, were involved in non-routine operations<sup>46</sup> by attempting to maintain steady-state operations, as the SOPs did not address handling flow restriction. In addition, they were unaware of the threat of liquid thermal expansion developing as a result of switching the cylinders and not evacuating the hoses after each switch-out operation.

#### **4.4 Process Hazard Analysis**

A team conducted a Process Hazard Analysis (PHA) on the phosgene cylinder feed system and vaporizer as part of the Front End SLM Unit assessment in 1994, 1999, 2004, and 2009. The 2009 PHA team, which included a senior process engineer, two technical resources, a mechanic, and a front end operator, all of whom were DuPont Belle employees, reviewed subtle changes to the process and associated MOC documentation since the last PHA in 2004, previous phosgene release incidents, and recommended corrective actions. The PHA for the phosgene system included the 1-ton cylinders, nitrogen pressuring

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<sup>46</sup> Non-routine operations are characterized by infrequent practice. Non-routine operations can be both planned and scheduled or can occur without an opportunity to schedule them.



system, the vaporizer, and all associated piping and controls. The team used a Hazard and Operability<sup>47</sup> (HAZOP) and “What If<sup>48</sup>” methodologies for the review of process hazards and deviations.

The team recognized and assessed the potential for a phosgene release from the cylinder transfer hoses but only if the hoses were incorrectly connected or inadvertently disconnected while the cylinder feed valve remained open. They did not assess the potential for the hose to rupture due to thermal expansion of liquid phosgene even though the potential for liquid phosgene thermal expansion was evaluated in other process equipment during the 2009 PHA.

None of the consequence scenarios the PHA team assessed involved failure of the phosgene transfer hose or the nitrogen flex hose. When it evaluated the phosgene vaporizer, the team considered corrosion potential when stainless steel is exposed to phosgene and water, but did not apply those factors to the cylinder transfer hoses. For the vaporizer, the probability value assigned to the phosgene leak scenario was decreased by reliance on the PM program to detect corrosion. The PHA team also noted that the slowly developing corrosion would decrease the probability of a leak because the corrosion would be noticeable during visual inspections. If the PHA team assessed the thermal expansion and corrosion issues for the phosgene transfer hoses and applied the same conditions to decrease the probability as used for the vaporizer corrosion scenario, the incident may still have occurred due to the team’s reliance on the preventative maintenance program to reduce the hazard. Unfortunately, the slowly developing corrosion on the hose was not visible due to the location of the clear plastic adhesive tape and the PM program was not configured to ensure that the hoses were changed at the appropriate frequency.

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<sup>47</sup> A systematic method in which process hazards and potential operating problems are identified using a series of guidewords to investigate process deviations (CCPS, 2008).

<sup>48</sup> A technique in which a team with process knowledge and experience examines possible process deviations or combinations of deviations than can result in an undesired consequence (CCPS, 2008).

Phosgene permeation through PTFE resulted in leaks at Belle in the past, however the PHA team did not consider this hazard for the phosgene cylinder hoses. The CSB received documentation of all SLM PHA audits dating back to 1994. The 1999 PHA included two incidents in which phosgene likely permeated through PTFE-lined conveyance equipment in other parts of the phosgene process. Even with these previous incidents taken into consideration, the PHA team still did not consider the potential for the phosgene cylinder hoses to result in a release under similar conditions.

## **4.5 Audits**

### **4.5.1 Unit Second-Party PSM Audit**

In August 2007, a second-party audit team comprised of engineers and health and safety experts from other DuPont facilities audited the SLM unit against regulatory and company PSM requirements. As in the F3455 unit audit, the team focused on MOC-subtle change, PSSRs, training, PHAs, mechanical integrity, and process technology. The audit contained 64 findings—27 observations, 35 policy, and 2 regulatory issues—for the Crop Protection business, consisting of the F3455 and SLM units at Belle.

One regulatory issue noted for the SLM and F3455 units was timely initiation of accident investigations. Auditors observed several instances where incident investigations were not started and communicated within the Belle Plant 24-hour or the 48-hour OSHA requirements. The audit team recommended revising the Belle Plant Incident Investigation procedure and area practices to ensure that plant personnel initiate investigations within 24 hours and no later than 48 hours following an incident. According to the audit tracking plan the CSB investigators reviewed, an assigned DuPont employee completed and closed the recommendation as of June 2009.

However, in the case of the hillside hose near-miss prior to the phosgene exposure (Section 4.3.3), operators told the CSB investigators that they planned to communicate the near-miss to supervisors for investigation the following Monday; however, this would not have been within the Belle Plant required 24-hour period. The OSHA PSM Standard requires the employer to “investigate each incident which

resulted in, or could reasonably have resulted in, a catastrophic release of highly hazardous chemical in the workplace” (1910.119(m)(1)) and that an incident investigation “shall be initiated as promptly as possible” (1910.119(m)(2)). Though supervisors are not typically present at the facility on weekends, management and safety and health experts, including the SLM Area Manager, were at the Belle Plant the morning of Saturday, January 23, 2010, attending the safety pause meeting. Had the incident been reported in a timely manner, management on site could have immediately initiated an investigation.

#### 4.5.2 On-Site Phosgene Generation

In 1988, DuPont engineers considered two options for using phosgene at the Belle facility: in cylinders from an off-site provider or making phosgene on-site by constructing a phosgene generation plant. To better understand the hazards involved in each design, DuPont engineers conducted a risk assessment in which four cases were considered Table 4:

- Case 1. Operating with a liquid phosgene feed from cylinders
- Case 2. Vaporizing the feed from the cylinders
- Case 3. Installing a plant to make phosgene from CO and Cl<sub>2</sub>
- Case 4. Enclosing the phosgene plant [in a fully contained building with an air scrubber]

After evaluating each case, they estimated the risk of fatality as follows:

	<b>On-Site Fatalities per 10,000 years</b>	<b>Off-Site Fatalities per 10,000 years</b>
Case 1	244	10.5
Case 2	154	0.22
Case 3	16.7	0.007
Case 4	2.3	0.006

Table 4. Preliminary Risk Assessment by DuPont Engineering, 1988 (Appendix E)

While it was estimated that Case 4 would have the least amount of risk, the assessment concluded,

“Spending \$2 MM for an enclosure to get from Case 3 to Case 4 saves 14.4 lives per 10,000 years. (Almost all the improvement is in on-site risk. Off-site risk

improvement is not significant.) This sets a value of life plus public outrage at \$143 MM.

It may be that in the present circumstances the business can afford \$2 MM for an enclosure; however, in the long run can we afford to take such action which has such a small impact on safety and yet sets a precedent for all highly toxic material activities [sic].”

After the analysis, construction on Case 3, the open to atmosphere phosgene generation plant, began. However, the phosgene generation plant was abandoned mid-construction, and Case 2 is the current configuration at the Belle facility.

Documentation to support why the phosgene generation plant was abandoned was not provided. The CSB obtained a proposal to DuPont by a third-party contractor to build the phosgene generation plant. The proposal for a plant, as presented in Case 3, estimated a cost of 830,000 dollars and stressed the contractor’s history of building successful phosgene generation units. DuPont decided not to act on this proposal. Anecdotal evidence from CSB interviews pointed to corporate engineers deciding to not hire a third party and using DuPont resources to construct the phosgene generation unit. However, once the project was partially complete, it was determined that the DuPont-designed system would not work, and the effort was abandoned.

DuPont made the decision to cancel plans for the enclosed phosgene generation unit, but the potential for offsite impact still remained a concern and was identified in SLM Unit PHAs years later. In 2004, Belle Plant personnel conducted a PHA on the SLM Unit and identified the need for a shed enclosure with a scrubber to mitigate or prevent the release of phosgene offsite. The recommendation was formed as a result of a “What if” analysis performed during the PHA. The PHA team listed two separate scenarios that could result in a plant-wide or offsite consequence, both recommending an enclosure to the shed. The original due date for the shed enclosure was scheduled for December 2005, but was extended. A

PHA recommendation extension request letter was created to describe the need for an extension and was signed by SLM Unit Management. The shed enclosure extension, scheduled for December 2006 was not met and there were three subsequent extensions on the enclosure recommendation which remained incomplete on the day of the fatal phosgene release (Table 5).

<b>PHA Enclosure Recommendation Delays</b>	
<b>2004</b>	
<p><b><u>Original Recommendation created in SLM 2004 PHA</u></b>                      "Provide appropriate mitigation to prevent multiple fatalities from the release of a 2000 lb phosgene cylinder."  <b>Due Date: Dec-05</b></p>	Dec-04
<b>2005</b>	
<p><b><u>First Extension</u></b>                      "A COC12 generation system is currently being evaluated, and if this was installed the shed enclosure may be designed differently to handle the appropriate chemicals."  <b>New Due Date: Dec-06</b></p>	May-05
<b>2006</b>	
<p><b><u>Second Extension</u></b>                      "Work to define the scope on this item is progressing but not yet complete. We are evaluating potential lower cost alternatives to total shed enclosure."  <b>New Due Date: Dec-08</b></p>	Dec-06
<b>2008</b>	
<p><b><u>Third Extension</u></b>                      "...the schedule indicates completion by August 2009."                      "The holds on the capital project were due to uncertainty of the future of the facility and due to the cost of the project."  <b>New Due Date: Nov-09</b></p>	Dec-08
<b>2009</b>	
<p><b><u>Fourth Extension</u></b>                      "... project to install a phosgene scrubber to address these recommendations, an error in basic data was discovered. This invalidated the original design basis for the scrubbing system, and required a halt to the project activity."  <b>New Due Date: Nov-10</b></p>	Nov-09
<p><b><u>SLM 2009 PHA Completed</u></b>                      32 Recommendations are made, none of which capture the outstanding recommendation from the SLM 2004 PHA</p>	Dec-09
<b>2010</b>	
<p><b><u>Fatal Phosgene Incident Occurs</u></b></p>	Jan-10

Table 5. PHA enclosure recommendation delays timeline

A year following the phosgene release incident, DuPont announced that it would idle the storage and use of phosgene at the Belle site, but did not state intentions for phosgene usage beyond 2011. The CSB requested documentation from DuPont that defines the status of the PHA recommendation for the shed enclosure as of the date of this report. DuPont extended the PHA recommendation for the shed enclosure for November 2010, but the shed was not enclosed prior to the deadline and extended again until the end of 2011.

#### 4.5.3 2006 Phosgene Committee Audit

In 2006, the Phosgene Guardian Committee audited against the DuPont Phosgene Highly Toxic Materials (HTM) Manual, which included a review of the phosgene cylinder storage shed, the SLM production area, and other areas of the Belle Plant. Three audit team members from other DuPont sites visited the Belle facility to conduct field walkthroughs and hold discussions with process unit personnel. The audit team divided the findings and recommendations from the audit into two categories: policies and observations. The policies were related to the requirements of the HTM manual and the observations were suggestions or preferred, but not mandatory, practices.

The team found no regulatory compliance deficiencies in the audit, but did issue five policy recommendations and eight observations to the Belle Plant. The policy findings applied to equipment downstream of the phosgene cylinder feed system, including a recommendation to add inspection plans for corrosion detection of the Teflon-lined reactor piping. The team found, and noted as an observation, that the hoses used on the phosgene feed system were not one of the three types of hoses recommended for phosgene service by the DuPont P3H Standard, but did not require the Belle facility to use the appropriate hoses.

The team also observed that liquid phosgene lines in the shed had moderate external corrosion and that significant moisture in the shed should be addressed to eliminate future corrosion potential. Because these items were observations, the HTM manual did not require that DuPont develop an action plan to resolve

them. The Belle plant continued to use a hose for phosgene service that the company standard did not recommend.

SLM unit equipment selection practices did not align with the requirements and recommendations in the phosgene HTM manual. The manual requires that “Materials of construction must be selected properly to handle phosgene safely” but only recommends against the use of nonmetals for piping, valves, and process equipment containing phosgene. It further states, “Where small amounts of phosgene are present, stainless steel lined with Teflon is commonly used” without specifically quantifying an amount of phosgene where Teflon is acceptable. In the SLM phosgene transfer system, phosgene was continuously present in the PTFE-lined hoses while the connected cylinder was feeding the process.

The HTM manual’s design information section requires that special attention be given to the, “prevention of over pressuring those lines and vessels where liquid phosgene can be trapped between two isolation valves.” In the course of switching between cylinders on the morning of the phosgene incident, SLM operators “blocked in” (i.e., closed the valve on each end of the hose), which trapped liquid phosgene between the partially filled riverside cylinder and the valve to the process. The liquid phosgene trapped in the hose underwent thermal expansion, rupturing the hose due to the overpressure of the line facilitated by the weakened and corroded stainless steel overbraid. None of the SOPs for the SLM unit warned against blocking in liquid phosgene to prevent hose ruptures, making operators less aware of the thermal expansion hazards of phosgene.

## **4.6 Standards and Guidelines**

### **4.6.1 DuPont Highly Toxic Materials Phosgene Manual**

The DuPont Highly Toxic Materials (HTM) Manual contains mandatory criteria for the storage, handling, maintenance, and management of phosgene in quantities with the potential to cause offsite impact if released. The 86-page manual also includes non-mandatory practices for new and existing units or facilities handling phosgene and company requirements and procedures related to first aid and medical



treatment, MOC, design information for new and existing phosgene equipment, and PSM principles. The Phosgene Guardian Committee reviews and revises the manual and the committee chairperson and Safety Health and Environmental (SHE) leader authorizes the revisions. The Responsible Care Core Team reviews and approves all changes to mandatory requirements before issuing the revised manual. The Plant or Unit Manager must authorize any deviation from the manual requirements before using an alternative practice. The HTM Committee conducts a safety analysis to ensure that the alternate practice is acceptable before implementation.

#### 4.6.2 American Chemistry Council (ACC) Phosgene Safe Practice Guidelines

Manufacturers and users of phosgene formed the Phosgene Panel in 1972 to share information about practices to safely produce, handle, and use phosgene throughout industry. The Phosgene Panel is part of the Chemical Products and Technology Division of the ACC, an industry trade association for chemical companies; its Chemical Products and Technology Division supports companies through continuous evaluation and communication improvements related to the safe use of hazardous chemicals. Engineers, health and safety experts, and occupational health physicians from member companies participate on the panel,<sup>49</sup> which meets twice a year to share information and experiences related to handling phosgene. The panel sponsors engineering studies and research to prevent phosgene-related incidents and has prepared manuals for phosgene safe practices and medical treatment information as a resource for ACC member companies.

The ACC Phosgene Panel compiles information from member companies into the *Phosgene Safe Practice Guidelines Manual* to provide general information to those that manufacture or handle phosgene. The manual contains nine sections of phosgene safety information such as phosgene properties, design

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<sup>49</sup> In 2010, all U.S. phosgene manufacturers participated in the panel: BASF Corp., Bayer Corp., Chemtura, Dow Chemical, DuPont, Huntsman, SABIC Innovative Plastics, and VanDeMark Chemicals, Inc.

information for phosgene process facilities, transportation, emergency planning, first aid and medical treatment, and training.

Phosgene panel members draft summaries of industry practices that they submit for review and approval by all members of the ACC Phosgene Panel prior to inclusion in the manual. The panel periodically updates the manual and adds new and relevant practices identified by industry. The ACC does not intend for the manual to be a training tool or be adopted as procedure; it is to be referenced for general information regarding safe practices for phosgene storage and use.

The “Design of Facilities” section of the manual has several subsections pertaining to construction materials and layout of phosgene process equipment and facilities. The section includes leak prevention information such as equipment inspections, monitoring, and alarms, and describes the use of engineering controls and multiple layers of protection or barriers between phosgene exposure hazards and personnel.

The section includes precautions with regards to piping and valves in phosgene service. The manual states that users should pay particular attention to:

- protecting piping from over-pressurization due to liquid phosgene trapped between closed valves;
- protecting dry<sup>50</sup> phosgene systems from the intrusion of moisture, which can react with phosgene and cause severe corrosion and failure; and,
- inspecting and testing where stainless steel materials are used to detect the presence of stress corrosion cracking caused by exposure to chlorides.

The section also states that the use of metallic and non-metallic hoses for permanent or temporary piping systems may increase the opportunity for phosgene leakage and advises users to give due consideration to

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<sup>50</sup> Phosgene in the absence of water or moisture, sometimes referred to as anhydrous.

the design, fabrication, and testing of all components. The manual also notes the potential permeability issue with PTFE liners and states that these liners are typically used for phosgene service in well-ventilated areas, but does not describe specifically what methods of ventilation are acceptable.

#### 4.6.3 National Fire Protection Association (NFPA)

The NFPA 55: *Compressed Gases and Cryogenic Fluids Code*, provides fundamental safeguards to users, producers, distributors, and others who handle compressed gas cylinders. The standard contains general requirements for storage, occupancy, and emergency response, as well as provisions for specific chemicals or hazard classes as defined by the NFPA. The current version of the CGA P-1 standard references NFPA 55 in the “Ventilation, Storage, and Site Criteria” section for toxic and corrosive gases.

DuPont Belle’s programs and practices related to the storage and handling of phosgene cylinders does not align with the provisions set forth in NFPA 55. NFPA 55 defines phosgene as a highly toxic gas because it contains a lethal concentration (LC<sub>50</sub>) equal to or less than 200 ppm in air when administered via inhalation for 1 hour.<sup>51</sup> The LC<sub>50</sub> for phosgene is 5 ppm for 1 hour of exposure (CGA P-20, 1995).

NFPA 55 includes guidelines for controls in buildings that store compressed gas cylinders, and classifies the phosgene shed structure as an indoor storage area because the walls comprise more than 25 percent of the shed perimeter (Figure 12). Indoor storage for the use of highly toxic gases must have a gas cabinet, exhausted enclosure, or a gas room, according to NFPA 55. Exhausted enclosures, gas cabinets, or gas rooms fully enclose cylinders and associated process equipment and are equipped with ventilation systems to capture and treat hazardous vapors. The phosgene shed at Belle, though considered indoor storage by NFPA, did not contain a ventilation system; instead, DuPont relied on natural ventilation from the outside to decrease concentrations of phosgene, which allowed phosgene vapors to travel downwind,

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<sup>51</sup> LC<sub>50</sub> is the lethal concentration for 50 percent of the exposed population.

potentially exposing other employees working outside. Without exhausted enclosures, no barriers were present to prevent phosgene from exposing operators or traveling off-site.

The standard also includes guidance for alarms to warn personnel of potential releases from compressed gas cylinders and associated equipment. The SLM unit at the Belle plant had alarms for phosgene releases that were activated manually by the control board operator upon notification from outside personnel or if a phosgene analyzer activated an alarm at the control board. NFPA 55 guidance states that manual emergency alarms should be provided in the buildings that enclose cylinders and, when activated, should sound local alarms to alert occupants in the surrounding area. The phosgene shed at Belle contains no alarms that can be activated locally. Operators suspecting a release are expected to communicate verbally with the control operator who then sounds an alarm. In the absence of automatic alarm notifications, personnel in the surrounding area risk exposure, as was the case on the day of the incident.

For gas detection systems, the NFPA states that alarms should activate a local alarm that is both audible and visual. In the phosgene shed, the SLM building area, and on the Belle Plant fence line, the gas detection systems activate alarms only in the SLM control room if concentrations exceed the alarm set points. The gas detectors do not locally sound or visually indicate the detection of a hazardous concentration to alert surrounding personnel.

#### 4.6.4 Compressed Gas Association (CGA) Standards for the Safe Handling of Cylinders

The CGA is an industry association that represents manufacturers, distributors, suppliers, and transporters of gases and cryogenic liquids. It develops and promotes standards and practices for the industrial and medical gas industry, with input from over 125 member companies. Standards include technical specifications, health and safety practices, and training and educational materials.

The VanDeMark phosgene bulletin references the current CGA Standard, Safe Handling of Compressed Gases in Containers (P-1), for the training and proper handling of phosgene cylinders. The P-1 Standard from 2008 includes safe practices related to the transportation, identification, and storage of compressed

gases and specific safe handling and storage rules for chemicals defined by hazard classes. Each chemical has an assigned hazard class based on its physical properties: flammable, asphyxiant, oxidizer, toxic, corrosive, and extreme cold. The CGA lists phosgene as a primary toxic and secondary corrosive. The toxic and corrosive gas section includes requirements for cylinder storage and ventilation, emergency response, and training. OSHA adopted the 1965 version of the CGA P-1 Standard under the requirements of the Compressed Gas Standard (29 CFR 1910.101). Under the OSHA Standard, the in-plant handling and storage of compressed gas cylinders shall be in accordance with CGA P-1 (1965).

The current version of the CGA P-1 standard includes a specific reference to Chapter 7 of NFPA 55 for the storage and handling of compressed gas cylinders with flammables, but only contains basic requirements for the storage and handling of corrosives and toxics. In CGA P-1 Section 6.2.6 of Flammable Gases, the standard includes NFPA 55 requirements such as separation distances, flammable storage quantities, and fire barriers. However for toxics, the P-1 Standard states, “Storage of corrosive and toxic gases shall be in accordance with local and/or provincial/territorial building and fire prevention codes.” The standard also states toxics “shall be filled and used only in adequately ventilated areas or preferably outdoors or in exhausted enclosures,” but does not contain any specific provisions to achieve adequately ventilated areas such as the requirements set forth in NFPA Section 7.9.

#### 4.6.5 CGA Standards for PTFE-lined Hoses

In 2010, CGA published the fourth edition of Standard E-9, Standard for Flexible, PTFE-lined Pigtailed<sup>52</sup> for Compressed Gas Service. Section 1 of E-9 states that the standard applies to hoses with a diameter of 0.25 inches or smaller and with a maximum allowable working pressure (MAWP) of at least 3,000 psi, such as the hoses used at DuPont. Section 2 of standard E-9 states, “PTFE-lined pigtailed are not suitable for use with... poisonous, toxic, or pyrophoric gases because permeation of gas through the PTFE wall

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<sup>52</sup> “Pigtails” are hoses or flexible tubing used to transfer material from a compressed gas cylinder.

creates a potential hazard.” Since phosgene is toxic, this standard rules out using PTFE-lined hoses for phosgene.

Additionally, Section 5 of Standard E-9 defines the identifying information for hoses, and rather than allowing tags with adhesive or heat-shrink wrap as was the case with the DuPont hoses, E-9 states, “The markings shall be made on the end fitting, collar, separate band, or other permanent location.”

The hose supplier’s practice of affixing adhesive tape on the hose itself did not align with the requirements in CGA E-9, and enhanced the corrosion of the metal braid on the PTFE-lined hoses at Belle. However, had DuPont followed this standard, they should have considered another non-permeable hose material as CGA prohibits the use of PTFE-lined hoses with permeable toxic gases such as phosgene.

The CGA 2008 P-1 Standard does not specifically reference the prior revisions of the E-9 standard. Section 5.9 of P-1 includes general requirements for container connections and states that “Piping, regulators, and other apparatus should be kept air tight to prevent leakage...” The P-1 Standard does not address materials of construction, or permeability for cylinder discharge hoses in the standard’s general requirements or the safe handling requirements by corrosive and toxic hazard class.

## **4.7 Key Findings**

1. An out-of-service phosgene transfer hose failed, exposing a worker to a lethal dose of phosgene.
2. DuPont did not follow its own standards for the change out of phosgene transfer hoses.
3. DuPont engineers voiced concerns regarding the materials of construction for phosgene hoses. These concerns were not addressed.
4. Liquid phosgene was not evacuated from the riverside hose, as the SOPs indicate, between transfers to the process from the 1-ton cylinders.

5. A similar hose failure almost occurred a few hours before the exposure of the worker, but the near-miss did not prompt an investigation when operators observed the failure mode on the morning of the fatal release.
6. The SAP maintenance program was altered so that a work order to change out the phosgene transfer hoses were no longer generated automatically (Appendix C).
7. one worker was confirmed to have been exposed to phosgene after the initial exposure while a second is thought to have been possibly exposed.
8. Emergency responders did not receive timely and detailed information on how to adequately prepare to respond to the incident.
9. There was no audible or visual phosgene alarm indication in or around the phosgene shed.
10. The 2009 PHA did not address thermal expansion and corrosion potential for phosgene transfer hoses.
11. Operators were unaware of the hazards of liquid phosgene thermal expansion (training and procedures).
12. No plant-wide notification occurred in response to the exposure.

## **4.8 Root Causes**

1. DuPont relied on a maintenance software program to initiate the automatic change-out of phosgene hoses at the prescribed interval.
2. DuPont did not provide a back-up method to ensure timely change-out of the hoses.
3. A maintenance software program change was not documented or reviewed in accordance with the MOC process.

4. No person with process knowledge was in place and assigned to convey timely and useful information to Metro 9-1-1. This responsibility was consigned to the gate guard.
5. The Belle Plant did not use the construction materials recommended by a corporate expert, the P3H standard, CGA or the HTM manual for phosgene hoses, even though the 2006 second-party HTM audit recorded it as an observation.

## 5.0 Three Incidents in 33 Hours

Because two incidents occurred in a relatively short period, on Saturday, January 23, 2010, after the oleum release had been secured, the Plant Manager convened a meeting of supervisors and roughly 10 managers and supervisors assigned to the Belle Plant Crisis Committee to discuss and initiate a safety pause, the intent of which was to evaluate what the managers had seen and “take appropriate steps to ensure safe operation.” Approximately 10 managers are part of the Crisis Committee, and after a debriefing, other supervisors and managers were advised that a safety pause would be conducted. Where possible, processes would be shut down to allow the discussion, and in those plants that could not be shut down, employees were expected to participate as best they could.

The Plant Manager assigned the Area Manager for the SLM and F3455 units (who was part of the Belle Plant Crisis Committee) to contact supervisors and managers and request that they come to the plant to participate in planning a plant-wide safety pause. These calls went out at about 11:00 a.m., and supervisors and managers started arriving at the plant at about noon. At about 2:00 p.m., shortly after the planning for the safety pause began, the group heard a radio call advising the plant of a medical emergency. In response to the Plant Manager’s inquiry, it was learned a worker had been exposed to phosgene in the SLM unit, making it the third incident in about 33 hours at the facility.

In a striking similarity of events and activities, after two release incidents at the Honeywell Baton Rouge facility in July 2003, upper management ordered the entire plant to shut down and review all facility



operations prior to re-start. During this safety stand-down, a third incident occurred where an employee was exposed to hydrofluoric acid during clean-up of an area in the plant.<sup>53</sup>

The objective of both shutdowns in these cases was to get the attention of the workforce, acknowledge that the occurrence of incidents was unacceptable, and to recommit to the two companies' respective core values of adhering to health and safety guidance. One common element was that both companies initiated safety stand-down activities after the string of incidents started in their respective plants. Another common theme was the precursor or near-miss events preceding actual incidents. At the Belle plant, even though investigations were conducted, near-miss investigations were not immediately responded to on weekends, including the near catastrophic failure of a separate phosgene transfer hose only hours earlier. Management at all levels are responsible for fostering an atmosphere of trust, openness, and encouragement of reporting near-misses and incidents, as failure to do so could result in non-reporting of near-miss events (CCPS, 1992). Despite these efforts to address the cause of the string of incidents at the Belle plants, a fatal incident occurred.

The examination of corporate oversight of safety management systems and corporate safety culture has been conducted as part of another CSB investigation of the BP Texas City incident in 2005<sup>54</sup>, and a blue ribbon panel of experts chaired by former Secretary of State James A. Baker was convened as the result of an urgent recommendation from that same investigation, *The Report of the BP U.S. Refineries Independent Safety Review Panel*. While not indicating that the work/safety culture was irretrievably broken at the Belle facility—and perhaps within the DuPont Corp.—the events before and after the string of incidents in late January 2010 suggest that the safety culture, has “shifted”, is not operating as it has

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<sup>53</sup> CSB-2003-13-I-LA (Honeywell).

<sup>54</sup> CSB 2005-04-I-TX, 2007

historically, and could benefit from an extensive examination of all facets of the safety culture, both within the facility and extending throughout the corporation.

### 5.0.1 Additional DuPont Incidents

About 8 months after the series of incidents at the Belle plant triggered this investigation, another significant release occurred. At about 4:00 p.m. on, September 21, 2010, DuPont Belle plant personnel discovered a methanol leak in a heat exchanger in the methylamines production unit while conducting regular sampling of the plant's water effluent stream. More than 160,000 pounds of methanol were estimated to have been released into the Kanawha River over a 24 hour period. This incident occurred when pressure on the process side of a heat exchanger was increased to a pressure greater than the steam condensate side of the process. After troubleshooting, operators suspected a leak on the process side of the heat exchanger, and increased steam pressure until samples of the effluent stream confirmed that the leak had stopped. No employee or community injuries were recorded as a result of this release.

Almost three months after the methanol release, on December 3, 2010 at about 2:23 a.m., a fume alert was sounded in the amines unit at the DuPont Belle, WV facility announcing a release of monomethylamine (MMA). The release occurred while two operators—one senior operator with 34 years of experience at DuPont and a junior operator with a little over one year's experience in the facility—were obtaining a sample of MMA from a rail car. One operator received 1<sup>st</sup> and 2<sup>nd</sup> degree chemical burns to his face, and one inhaled some of the escaping MMA in addition to receiving 1<sup>st</sup> degree chemical burns to his face. Both were transported to Charleston Area Medical Center for 24-hour treatment and observation and were released the following day.

CSB investigators returned to the Belle facility to conduct an assessment of this incident. In examining the equipment, one area of concern was the design of the valves used to isolate the sampling apparatus. As configured during the sampling operation, only a single block valve isolated the process from the sample container. This is in contrast to industry standards which suggest the use of double block valves

and bleed vents to allow assurance that the sample piping is clear of hazardous material prior to disconnecting. About 10 pounds of MMA are estimated to have been released during this incident, and no complaints were received from the community.

At DuPont's Yerkes facility, in Tonawanda, NY, the CSB conducted an assessment of a hot work incident that caused a fatality to a welder and an injury to his supervisor on November 9, 2010. This incident was under investigation as this report went to publication, but preliminary assessments indicated that pre-hot work inspections were less than adequate, including a failure to check the atmosphere in a tank that normally processed non-flammable material, but that had inter-connecting piping that could route flammable vinyl fluoride into the tank. The workers were assigned to make repairs to the tank, but prior to commencing their work there is no record of DuPont using a portable gas detector to ensure that the tank being worked on was free of flammable material.

## **5.1 Management Systems**

### **5.1.1 Knowledge Management**

DuPont employees told the CSB investigators that many "very knowledgeable" Belle plant operations and maintenance workers had recently retired or are approaching retirement age. From 2005 to the end of 2009, 82 Belle Plant employees retired and 14 resigned. The total number of employees at the Belle plant has dropped 13 percent (55 people) over the last 5 years. A loss of plant-specific knowledge, or "corporate memory fade" has contributed several incidents in industry (CCPS, 1995), as new hires cannot replace years of experience; thus, companies must train and supervise new staff until they acquire job competencies to work safely.

Experienced maintenance mechanics and technicians have valuable hands-on experience and knowledge of equipment essential to the safe operation of plant processes. A worker in the Belle maintenance department told the CSB investigators that they reported to four different maintenance site leaders over

the last 5 years prior to the January 2010 incidents. Other employees expressed concerns that new hires spent too little time learning from veteran employees.

The CSB investigators reviewed and compiled workforce data from DuPont Belle organization announcements between January 2005 and June 2010, which listed all new hires, transfers, resignations, and retirements that affected the Belle workforce. Over the 4 years, there were 85 retirements totaling 2,572 years of experience with an average of 30 years of service per employee. Among the 85, 20 were from the maintenance department, contributing to a loss of 713 total years of knowledge and experience (Table 6).

<b>DuPont Belle Workforce 2005 to 2009</b>		
Retirements		Years experience at Belle
Maintenance	20	713
Total	85	2,572
New hires		Years experience at Belle
Maintenance	10	0
Total	101	0

Table 6. Sum of Belle plant retirements and new hires from 2005 to 2009<sup>55</sup>

In addition to the 85 retirements, there were 14 resignations and 14 transfers to other sites. The Belle plant hired 101 new employees over that four-year period and 8 DuPont employees transferred to Belle from other sites. Though the overall proportion of new to departing employees has remained consistent, a significant reduction of employees with an average of 30 years of experience working on the Belle site contributes to a loss of institutional and plant-specific knowledge.

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<sup>55</sup> This does not include interns, co-ops, special assignments, or leaves of absence.

In the case of Belle, a significant population of employees is retiring, with a great deal of process knowledge that is lost if not properly maintained. This is an issue for industry in general as an entire generation of baby boomers approaches retirement. In January, 2011, DuPont announced plans to hire 150 employees at Belle over the next few years to compensate for the number of retiring workers.

### 5.1.2 Hierarchy of Controls

The Hierarchy of Controls is a method generally recognized and used by health and safety professionals to control workplace hazards. The National Safety Council (NSC) developed the Hierarchy of Controls in the 1950s and Congress later adopted and enacted it into the Occupational Safety and Health Act of 1970. The Hierarchy of Controls (Figure 17) demands the use of higher-level engineering and administrative controls to eliminate hazards. When those operations are not feasible, a PPE program must be implemented.

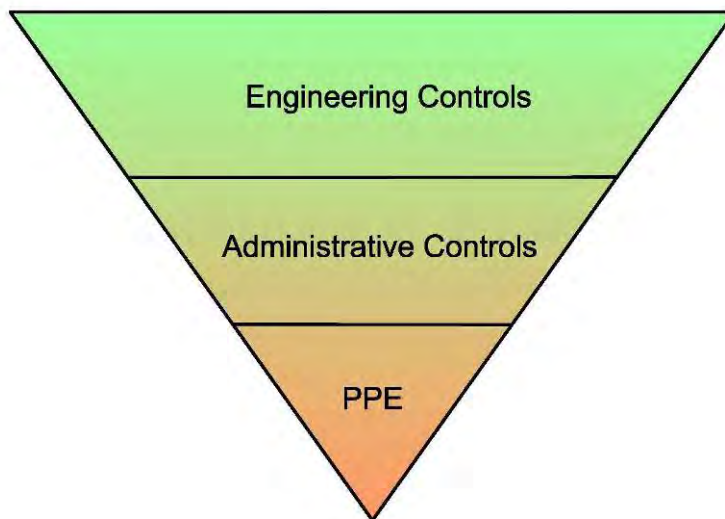


Figure 17. Hierarchy of Controls

DuPont recognized the notion of eliminating hazards in the early 1900s as the preferred method beyond education and protection. However, operating procedures for the SLM phosgene cylinder feed system relied primarily on work practices and PPE to protect operators from the exposure hazards on the day of

the incident. Other facilities within DuPont and in the chemical industry have engineering controls in place for similar phosgene cylinder operations.

#### 5.1.2.1 Design and Engineering Controls for Phosgene Cylinders

In 1984, employees at the Ciba-Geigy Corp. published a technical paper about the safe handling of phosgene in chemical processing specific to the operation of 1-ton phosgene cylinders (Alspach et al., 1984). Ciba-Geigy, now part of BASF, had a facility in Toms River, NJ, where two 1-ton cylinders of phosgene fed a chemical process. Similar to DuPont, the cylinders connected to the process through PTFE-lined hoses with a stainless steel overbraid induced with nitrogen to drive liquid from the cylinders. At the Ciba-Geigy plant, a transparent isolation chamber enclosed the cylinder valve connections and operators opened and closed valves while standing outside the enclosure, extending their arms through rubber arms and gloves that were part of enclosure. The enclosure continuously vented to a caustic scrubber and acted as a barrier between the operator and any potential phosgene vapors present near the cylinders.

The phosgene area had phosgene analyzers to continuously monitor and alarm if concentrations exceeded a defined set point. At high concentrations, alarms would automatically alert the production building, plant guards, and adjacent roadways and buildings with flashing lights and audible warnings. At the Belle facility, phosgene readings on the analyzers activate alarms in the control room, but DuPont relies on the board operator to notify personnel in the unit and the rest of the plant. By automating the phosgene analyzer alarm system to activate notifications plant-wide, Ciba-Geigy eliminated the reliance on work practices to notify and protect personnel.

#### 5.1.2.2 Phosgene Handling at the DuPont Mobile, AL Plant

The DuPont Mobile plant in Mobile, AL, uses the same 1-ton phosgene cylinders as Belle for its agricultural chemicals process. The Mobile process has three cylinders on weigh scales, transferred to the process through similar PTFE-lined flexible hoses with a stainless steel overbraid made by a different

manufacturer. The Mobile hoses are 18 inches shorter and have a greater maximum operating temperature and pressure than those used at Belle. A hose distributor supplies both hoses from the manufacturer to each site.

The phosgene cylinders and weigh scales at the Mobile plant are housed in an enclosed room. The cylinder room vents to an emergency scrubber that pulls a slight negative pressure on the room and scrubs air before venting to the atmosphere. The scrubber is designed to capture vapors from a release of an entire cylinder. Operators at the Mobile plant enter the phosgene cylinder area under the same PPE requirements as Belle for isolating and changing cylinders (hard hat, steel-toed shoes, safety glasses, and phosgene dosimeter). However, at Mobile, to capture and scrub phosgene vapors in the event of a release, the operator turns on the emergency scrubber and pump before entering the enclosure.

Like Belle, Mobile has phosgene analyzers located in and around the unit to continuously monitor concentrations. At Mobile, alarms in the cylinder enclosure activate local audible alarms inside the enclosure and a flashing light outside to alert employees. If no operators are present in the enclosure when the alarm activates, the emergency vent scrubber automatically starts. The Belle plant analyzer in the phosgene shed had no audible alarm to alert personnel in the area; instead, Belle plant procedures require the board operator to notify personnel of the release and only operators at the phosgene shed can activate the switch for the warning light.

The emergency scrub system and automated alarms at Mobile are examples of higher-level controls that protect workers from hazards. Mobile has automated alarms where Belle relies on operator action to initiate alarms to warn personnel of a suspected or actual release. Mobile implemented the scrubber system, an example of an engineering control, to manage the concentrations of phosgene in the cylinder enclosure in the event of a release. The Belle plant phosgene shed design allows only for natural ventilation to carry unwashed phosgene gases that can potentially harm personnel in or around the shed and possibly enter the community.

### 5.1.2.3 Safety in Design Issues

Safety considerations in the equipment design stage eliminate the need for companies to retrofit existing process equipment or implement administrative or PPE programs to protect workers and the environment.

In addition to the SLM unit, the CSB also identified a lack of safety and health considerations during the design and construction phases of the F3455 and SAR units. In the F3455 unit, engineers did not design the control system alarms so that operators could distinguish between a failed battery and activation of a rupture disc burst sensor, which resulted in nuisance alarms for the rupture disc on the methyl chloride vent line. Instead of addressing the reliability issues associated with the frequently failing sensor, management decided to wire the burst sensor to electric power so that low batteries were no longer causing frequent and false alarms. However, operators were not retrained to respond to the alarm causing them to disregard the alarm during the F3455 unit maintenance activity; consequently, the unit restarted with a failed rupture disc.

CSB investigators also noted safety in design issues with the presence of the weep hole on the methyl chloride vent line upstream of the rupture disc assembly. DuPont engineering standards require that drainage holes be placed upstream of the relief devices on vent lines to allow for drainage and prevent liquid from lodging in the discharge side of the rupture disc. However, the location of the weep hole allowed toxic vapors from the methyl chloride vent line to enter the F3455 building where concentrations could accumulate to dangerous levels. DuPont could have designed the vent line so that the weep hole would drain to the exterior of the facility, where vapors would dissipate into the atmosphere in the event of a burst rupture disc.

In the SAR unit, DuPont chose copper steam tracing to prevent the oleum sample line and other process lines from freezing even though steam tracing is not the preferred method for oleum service (Dillon, 1997). Steam tracing can create hot spots that result in an uneven heat distribution in the oleum sample line, which can accelerate corrosion. The use of steam tracing in the SAR unit exacerbated the corrosion incident in the oleum sample line, resulting in a significant release of oleum. Had the SAR unit design



engineers called for electric tracing or replaced the steam tracing, the larger hole in the sample line might not have formed.

## **6.0 Regulatory Analysis**

### **6.1 Occupational Safety and Health Administration (OSHA)**

#### **6.1.1 Process Safety Management Program**

The OSHA PSM Standard (29 CFR 1910.119) requires employers to minimize or prevent the consequence of catastrophic incidents involving highly hazardous chemicals by applying elements of the PSM regulation to covered processes. PSM applies to processes using or producing any of the 137 listed toxic chemicals at or above threshold quantities and processes with flammable liquids or gases onsite in quantities of 10,000 pounds or more in one location. The PSM Standard applies to the SLM and F3455 units because they contain listed toxic chemicals in excess of the threshold quantities (TQ) specified in the regulation.

A Process Hazard Analysis (PHA) is one of the 14 elements in the PSM Standard requiring the employer to assess all PSM-covered processes to identify, evaluate, and control hazards involved in the processes by using one or a combination of several methodologies listed in the regulation. Furthermore, the standard requires the PHA to address<sup>56</sup>

- the hazards of the process
- engineering and administrative controls applicable to the hazards and their interrelationships such as appropriate application of detection methodologies to provide early warning of releases
- consequences of failure of engineering and administrative controls

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<sup>56</sup> 29 CFR 1910.119(e)(3).

In the 2009 PHA for the SLM unit, the team did not assess the potential for a phosgene release from a failed transfer hose due to corrosion or thermal expansion but did consider these issues in process equipment downstream of the hoses. The team identified engineering and administrative controls, such as the PM system and adherence to SOPs, to reduce the likelihood of a phosgene release from this equipment. However, the team did not assess the consequences caused by the preventative maintenance system failing to initiate hose replacements at the proper frequency. In its 2009 PHA for the SLM unit, an audit team did not address phosgene thermal expansion in the liquid transfer hose; consequently, in July 2010, OSHA issued a serious violation to DuPont.

The PSM Standard also requires employers to conduct an MOC for all modifications to process chemicals, technology, equipment, and procedures; and changes to facilities that affect a PSM-covered process. The procedures are meant to address the following prior to the change<sup>57</sup>:

- The technical basis for the proposed change
- Impact of change on safety and health
- Modifications to operating procedures
- Necessary time period for the change
- Authorization requirements for the proposed change

The MOC also requires that the employees in operations and maintenance affected by the change be informed of the change and trained prior to the start-up of that process.

Investigators found MOC program deficiencies for modifications made to critical equipment on both the F3455 and SLM units. On the F3455 unit, DuPont's MOC process approved a design for the rupture disc alarm system that lacked sufficient reliability to minimize the release of flammable methyl chloride. The unit changed the rupture disc burst sensor on the methyl chloride vent line from battery power to electric

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<sup>57</sup> 29 CFR 1910.119(l).

to eliminate battery failure, but failed to assess the reliability of the burst sensors individually. The MOC process did not evaluate the basis of the modification to verify that it met the intended purpose of eliminating nuisance alarms caused by battery failure.

DuPont did not perform an MOC review for the changes to the maintenance system that handled the phosgene hose replacements on the SLM unit. The modification made to the phosgene hose replacement work orders kept the system from generating a new work order, thus extending phosgene hose use beyond its planned service life. DuPont stated that knowledge of the change was limited to only a few key SAP users, but they lacked training necessary to recognize its impact on hose replacement frequency.

### 6.1.2 Compressed Gases

The OSHA Standard for Compressed Gases (29 CFR 1910.101) applies to employers that handle, store, and use compressed gases in cylinders, portable tanks, or tank cars. The standard includes requirements for cylinder inspections, safety relief devices, and storage and handling of compressed gas cylinders and requires employers to handle and store cylinders in accordance with CGA pamphlet P-1 1965, "Safe Handling of Compressed Gases in Containers."

In the 41 years since OSHA adopted the reference standard as part of the Compressed Gas Regulation, CGA P-1 has been revised 10 times. The current 2008 version of the P-1 Standard is more comprehensive than the OSHA-adopted 1965 version. The 1965 version does not list chemicals by hazard class and contains only specific safety information for flammable and poisonous gases. The current version lists 82 chemicals that fall into the primary toxics category, whereas the 1965 version lists only 13 poisonous gases as defined by the Interstate Commerce Commission (ICC).<sup>58</sup> The 1965 standard contains the same general information as the current version, but lacks the detailed guidance for facility siting,

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<sup>58</sup> A regulatory body abolished in 1995 some of whose responsibilities were transferred to the Surface Transportation Board, an agency within the U.S. Department of Transportation.

emergency response, and safety information specific to various types of chemicals stored in compressed gas cylinders. The 1965 version includes obsolete and outdated references and lacks references to applicable OSHA regulations, as it was published prior to the establishment of OSHA. With respect to the issues identified in the phosgene release investigation, had OSHA adopted the current version of the CGA P-1 Standard, DuPont would have been accountable for more phosgene storage engineering controls by the incorporation of NFPA 55 and other consensus standards referenced in the standard.

### 6.1.3 Inspection History

OSHA is authorized under the Occupational Safety and Health Act of 1970 to conduct workplace inspections to ensure that employers are providing a safe and healthy work environment by complying with standards issued by the agency. A range of inspection categories establish a system of priorities:

- Imminent Danger
- Catastrophes and Fatal Accidents
- Complaints and Referrals
- Programmed Inspections
- Follow-up Inspections

A review of OSHA's inspection history reveals that three planned inspections were conducted at the Belle facility in 1982, 1984, and 1993, in addition to one unprogrammed-related<sup>59</sup> inspection in 1981. Even though no planned inspections took place from 1993 through 2010, two inspections in 1995 and one in 2004 were the result of complaints, all of which were closed.

In a series of post-incident inspections, OSHA cited DuPont for a serious violation of Section 5(a)(1) of the Occupational Safety and Health Act, alleging that inspections were not conducted for all sections of

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<sup>59</sup> An unprogrammed-related inspection can occur at a multi-employer worksite when an employer is being inspected because of a complaint, accident, or referral. Any other employer with workers on the worksite is subject to inspection.

oleum piping based on prior leak incidents at the SAR unit. Citations for numerous violations of the PSM<sup>60</sup> Standard were also issued. OSHA cited DuPont for serious violations, including the company's failure to properly inspect piping used to transfer phosgene, perform a thorough PHA for its phosgene operation, and train workers on hazards associated with phosgene. The OSHA PSM Standard (29 CFR 1910.119) requires employers to prevent or minimize the consequences of a catastrophic release of highly hazardous chemicals as well as flammable liquids and gases. Phosgene and methyl chloride are listed chemicals, and the SLM and F3455 units processed more than the TQ, so the PSM Standard applied. Proposed penalties for all violations totaled \$43,000.

## 6.2 Environmental Protection Agency

The EPA Risk Management Program (RMP) regulation (40 CFR 68), mandated by Section 112(r) of the Clean Air Act Amendments of 1990, regulates the use of highly hazardous chemicals at fixed facilities. Its purpose is to prevent accidental offsite releases of listed substances and ensure that a company and the community are able to respond effectively in the event of a release. The regulation applies to facilities using or storing regulated substances exceeding the TQ specified in the EPA regulations.

Each covered process is required to be designated as one of three “prevention program” levels based on offsite consequence analyses, incident history, and PSM program applicability. Program 1 is the lowest, simplest management program; Program 2 is an intermediate management-level program with added program elements and basic documentation requirements. PSM-covered processes cannot be designated Program 2. Program 3 is the highest-level management program; most PSM-covered processes fall into Program 3, which requires a rigorous management program with detailed record retention criteria and all PSM program elements. All PSM program activities and records are directly applicable to the Program 3

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<sup>60</sup> PSM is a regulation promulgated by OSHA. A process is any activity or combination of activities including any use, storage, manufacturing, handling or the on-site movement of HHCs as defined by OSHA and the EPA.

regulatory activities, and all RMP covered chemicals at the DuPont Belle plant fall into Program 3 requirements (Table 7).

<b>Toxics</b>	<b>RMP TQ (lbs)</b>
Anhydrous Ammonia	10,000
Phosgene	500
Sulfur Trioxide	10,000
Formaldehyde	15,000
Oleum	10,000
Methyl Chloroformate	5,000
<b>Flammables</b>	
Dimethylamine	10,000
Methylamine	10,000
Methyl Ether	10,000
Ethylamine (70% aqueous)	10,000

Table 7. DuPont Belle RMP-covered chemicals and threshold quantities

Each covered process must undergo a hazard assessment (40 CFR 68, Subpart B) in which the owner is required to prepare a “worst case release scenario” and an “alternative release scenario” for each covered process. Different analysis criteria apply based on whether the covered chemical is toxic or flammable. The hazard assessment also requires inclusion of the “five year accident history.” The results of the hazard assessment, along with other pertinent information for each covered process, must be submitted to the EPA. The Risk Management Plan (40 CFR 68, Subpart G) is submitted electronically and must be periodically updated. The DuPont Risk Management Plan submission for 2010 had no accident history to report.

In November 2003, the EPA Region III Chemical Accident Prevention Program audited the Belle facility to ensure compliance with the EPA RMP. The EPA audited the 2-million gallon ammonia storage tank against the RMP requirements for Program 3 management programs and the Risk Management Plan documentation DuPont submitted. The audit covered all RMP elements and emergency response and site security. The EPA audit report submitted to DuPont in December 2003 contained no deficiencies or

recommendations for improvement. The November 2003 RMP audit is the only one conducted at the Belle Plant prior to the January 2010 incidents.

### **6.3 State Hazardous Chemical Release Prevention Program**

On January 20, 2011, the CSBs Bayer CropScience investigation issued a recommendation to the Kanawha-Charleston Health Department to establish a Hazardous Chemical Release Prevention Program with the objective of enhancing the prevention of accidental releases of highly hazardous chemicals and optimizing responses in the event of their occurrence. In light of its proximity in the Kanawha Valley, the series of incidents at the DuPont Belle, WV facility support the plant's inclusion in such a program.

The implementation of the new program would incorporate several key guidelines applicable to chemical plants operating in the Kanawha County. The Belle facility is one of 13 facilities in the county that report EPA Risk Management Program covered chemicals assigned as Program level 3 that could fall under the auspices of the program. The recommendation to the Kanawha-Charleston Health Department stated:

*Specifically, the Bayer report recommends that the Director of the Kanawha-Charleston Health Department establish a Hazardous Chemical Release Prevention Program to enhance the prevention of accidental releases of highly hazardous chemicals, and optimize responses in the event of their occurrence. In establishing the program, study and evaluate the possible applicability of the experience of similar programs in the country, such as those summarized in Section 5.3 of this report. As a minimum:*

- a. Ensure that the new program:*
  - 1. Implements an effective system of independent oversight and other services to enhance the prevention of accidental releases of highly hazardous chemicals*
  - 2. Facilitates the collaboration of multiple stakeholders in achieving common goals of chemical safety; and,*

3. *Increases the confidence of the community, the workforce, and the local authorities in the ability of the facility owners to prevent and respond to accidental releases of highly hazardous chemicals*
- b. *Define the characteristics of chemical facilities that would be covered by the new Program, such as the hazards and potential risks of their chemicals and processes, their quantities, and similar relevant factors;*
- c. *Ensure that covered facilities develop, implement, and submit for review and approval:*
  1. *Applicable hazard and process information and evaluations.*
  2. *Written safety plans with appropriate descriptions of hazard controls, safety culture and human factors programs with employee participation, and consideration of the adoption of inherently safer systems to reduce risks*
  3. *Emergency response plans; and,*
  4. *Performance indicators addressing the prevention of chemical incidents.*
- d. *Ensure that the program has the right to evaluate the documents submitted by the covered facilities, and to require modifications, as necessary*
- e. *Ensure that the program has right-of-entry to covered facilities, and access to requisite information to conduct periodic audits of safety systems and investigations of chemical releases;*
- f. *Establish a system of fees assessed on covered facilities sufficient to cover the oversight and related services to be provided to the facilities including necessary technical and administrative personnel; and,*
- g. *Consistent with applicable law, ensure that the program provides reasonable public participation with the program staff in review of facility programs and access to:*
  1. *The materials submitted by covered facilities (e.g., hazard evaluations, safety plans, emergency response plans);*



2. *The reviews conducted by program staff and the modifications triggered by those reviews;*
3. *Records of audits and incident investigations conducted by the program;*
4. *Performance indicator reports and data submitted by the facilities, and;*
5. *Other relevant information concerning the hazards and the control methods overseen by the program.*

*Ensure that the program will require a periodic review of the designated agency activities and issue a periodic public report of its activities and recommended action items.<sup>61</sup>*

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<sup>61</sup> CSB-2008-I-WV (Bayer CropScience)

## 7.0 Recommendations

The CSB makes recommendations based on the findings and conclusions of its investigations.

Recommendations are made to parties that can effect change to prevent future incidents, which may include the companies involved; industry organizations responsible for developing good practice guidelines; regulatory bodies; and/or organizations that have the ability to broadly communicate lessons learned from the incident, such as trade associations and labor unions.

### Phosgene Exposure

#### The Occupational Safety and Health Administration (OSHA)

2010-06-I-WV-R1

Revise the OSHA 29 CFR 1910.101, *General Industry Standard for Compressed Gases*, to require facilities that handle toxic and highly toxic materials in compressed gas cylinders to incorporate provisions that are at least as effective as the 2010 edition of Section 7.9, *Toxic and Highly Toxic Gases*, in National Fire Protection Association (NFPA) 55, *Compressed Gases and Cryogenic Fluids Code*, including enclosures, ventilation and treatment systems, interlocked fail-safe shutdown valves, gas detection and alarm systems, piping system components, and similarly relevant layers of protection.

2010-06-I-WV-R2

Take sustained measures to minimize the exposure of hazards to workers handling highly toxic gases from cylinders and associated regulators, gages, hoses, and appliances. Ensure that OSHA managers, compliance officers, equivalent state OSHA plan personnel and regulated parties conform, under the *Process Safety Management Standard* (29 CFR 1910.119) Recognized And Generally Accepted Good Engineering Practices (RAGAGEP) provisions, to industry practices at least as effective as the following:

1. NFPA 55 - *Compressed Gases and Cryogenic Fluids Code* (2010)
2. CGA P-1 *Safe Handling of Compressed Gases in Containers* (2008)
3. CGA E-9 *Standard for Flexible, PTFE-lined Pigtailed for Compressed Gas Service* (2010)
4. ASME B31.3 *Process Piping* (2008)

## DuPont Belle Plant

2010-06-I-WV-R3

Improve the existing maintenance management by:

- Supplementing the computerized system with sufficient redundancy to ensure tracking and timely scheduling of preventive maintenance for all PSM-critical equipment.
- Conducting Management of Change (MOCs) reviews for all changes to preventive maintenance orders for all PSM-critical equipment in the computerized maintenance management system.

2010-06-I-WV-R4

Revise the facility emergency response protocol to require that a responsible and accountable DuPont employee always be available (all shifts, all days) to provide timely and accurate information to the Kanawha County Emergency Ambulance Authority (KCEAA) and Metro 9-1-1 dispatchers.

2010-06-I-WV-R5

Revise the near-miss reporting and investigation policy and implement a program that includes the following at a minimum:

- Ensures employee participation in reporting, investigating, analyzing and recommending corrective actions as appropriate for all near-misses and disruptions of normal operations.

- Develops and encourage use of an anonymous electronic and/or hard copy near-miss reporting process for all DuPont Belle site employees.
- Establishes roles and responsibilities for ownership, management, execution, and resolution of recommendations from incident or near-miss investigations at the DuPont Belle facility.
- Ensures that the near-miss investigation program requires prompt investigations, as appropriate, and that results are promptly circulated to well suited recipients throughout the DuPont Corporation.
- Ensures that this program is operational at all times (e.g. during night, weekend, and holiday shifts).

## **E.I. DuPont de Nemours and Co., Inc.**

2010-06-I-WV-R6

Revise safeguards for phosgene handling at all DuPont facilities by:

- Requiring that all indoor phosgene production and storage areas, as defined in NFPA 55, have secondary enclosures, mechanical ventilation systems, emergency phosgene scrubbers, and automated audible alarms, which are at a minimum consistent with the standards of NFPA 55 for highly toxic gases.
- Prohibiting the use of hoses with permeable cores and materials susceptible to chlorides corrosion for phosgene transfer
- Conducting annual phosgene hazard awareness training for all employees that handle phosgene, including the hazards associated with thermal expansion of entrapped liquid phosgene in piping and equipment

2010-06-I-WV-R7

Conduct a review of all DuPont units that produce and handle phosgene. At minimum this review shall observe and document site-specific practices for engineering controls; materials of construction; PPE; procedures; maintenance; emergency response; release detection and alarms, and utilize information from sources outside of the company to develop and implement consistent, company-wide policies for the safe production and handling of phosgene.

2010-06-I-WV-R8

For each DuPont facility that uses, but does not manufacture phosgene on-site:

- Conduct a risk assessment of manufacturing phosgene on-site against the current configuration
- Communicate the findings of each assessment to compile recommendations applicable to all DuPont phosgene delivery systems
- Implement these recommendations

### **Compressed Gas Association, Inc.**

2010-06-I-WV-R9

Revise CGA P-1 *Safe Handling of Compressed Gases in Containers* to include specific requirements for the storage and handling of highly toxic compressed gas including enclosure ventilation and alarm requirements at least as protective as Section 7.9 Toxic and Highly Toxic Gases, NFPA 55 *Compressed Gases and Cryogenics Fluids Code*.

2010-06-I-WV-R10

Revise CGA P-1 *Safe Handling of Compressed Gases in Containers* to incorporate by reference the CGA E-9 Standard for Flexible, PTFE-lined Pigtailed for Compressed Gas Service.

## American Chemistry Council Phosgene Panel

2010-06-I-WV-R11

Revise the *Phosgene Safe Practice Guidelines Manual* to incorporate the following:

- Advise against the use of hoses for phosgene transfer that are constructed from permeable cores and materials subject to chlorides corrosion.
- Include guidance for the immediate reporting and prompt investigation of all potential (near miss) releases of phosgene.

## Methyl Chloride Release

### E.I. DuPont de Nemours and Co., Inc.

2010-06-I-WV-R12

Commission an audit in consultation with operations personnel to establish and identify the conditions that cause nuisance alarms at all DuPont facilities. Establish and implement a corporate alarm management program as part of the DuPont PSM Program, including measures to prevent nuisance alarms and other malfunctions in those systems. Include initial and refresher training as an integral part of this effort.

2010-06-I-WV-R13

Revise the DuPont PSM standard to require confirmation that all safety alarms/interlocks are in proper working order (e.g., not in an *active* alarm state) prior to the start-up of all Higher-Hazard Process facilities.

2010-06-I-WV-R14

Reevaluate and clarify the DuPont corporate Management of Change (MOC) policies to ensure proper identification and use by staff of the distinctions between subtle and full changes, and train

the appropriate personnel in the proper application of the distinctions and any changes in the policy.

By the

U.S. Chemical Safety and Hazard Investigation Board

Dr. Rafael Moure-Eraso

Chair

John Bresland

Member

Mark Griffon

Member

William Wark

Member

William Wright

Member

Date of Board Approval



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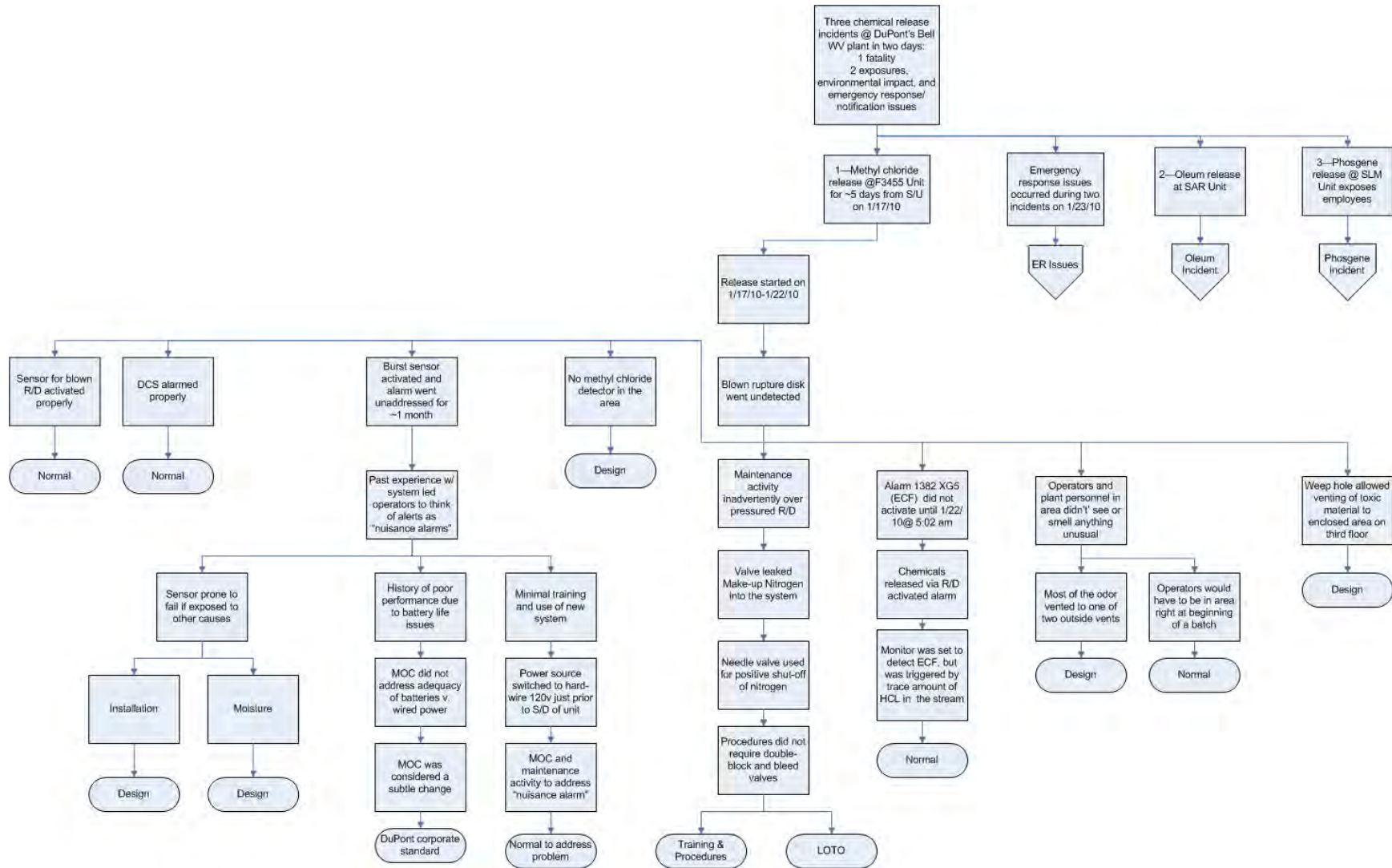
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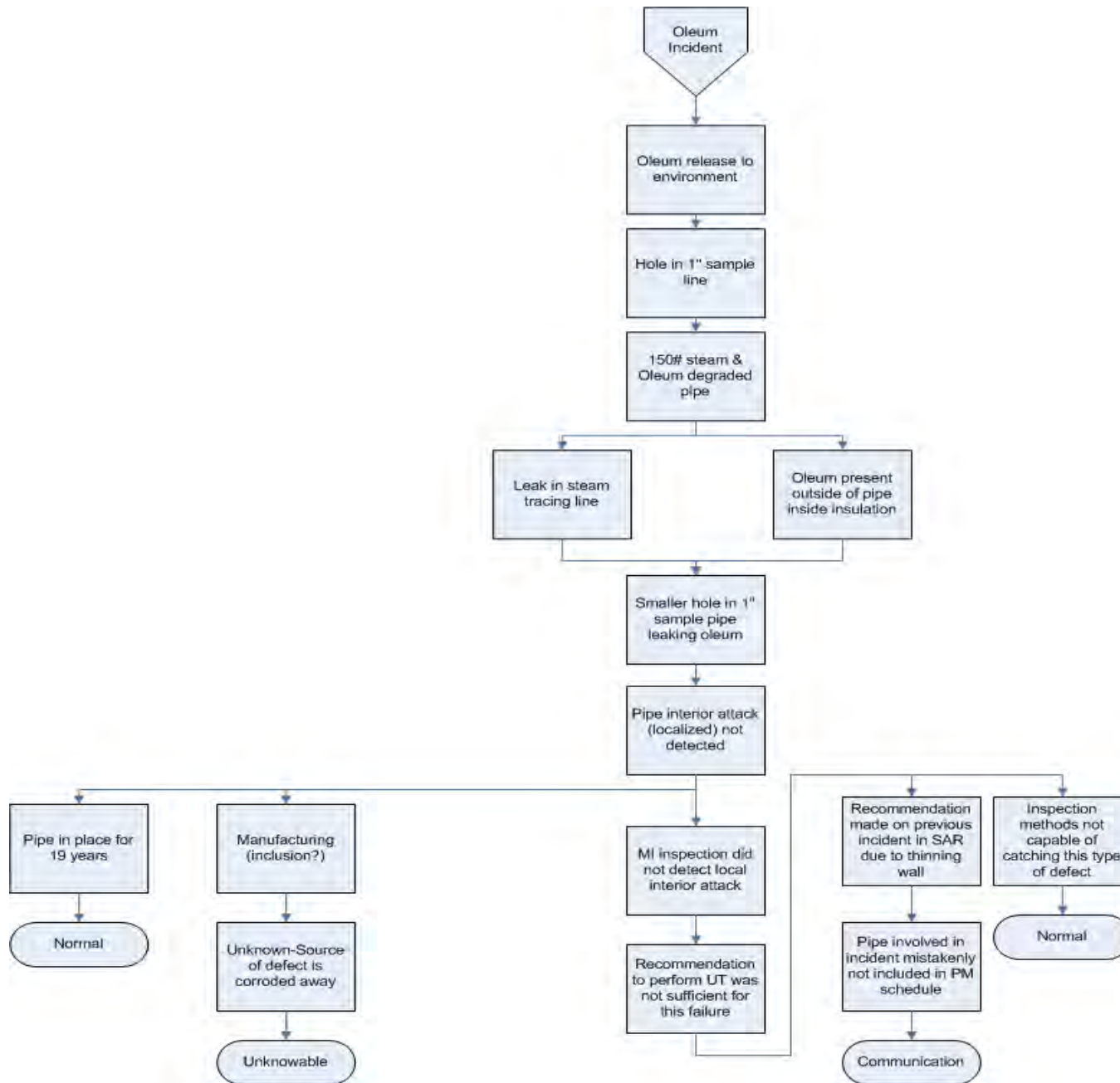
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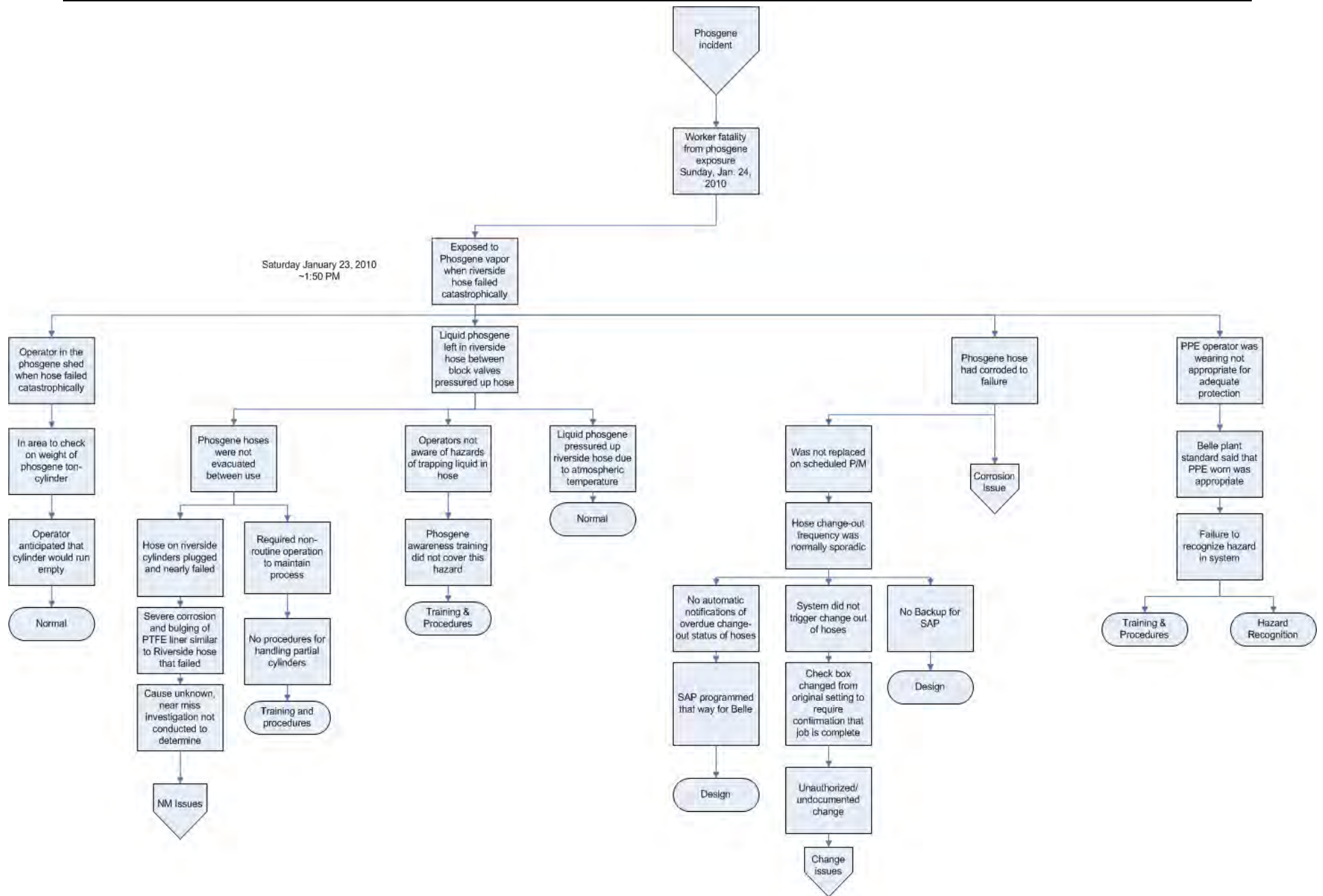
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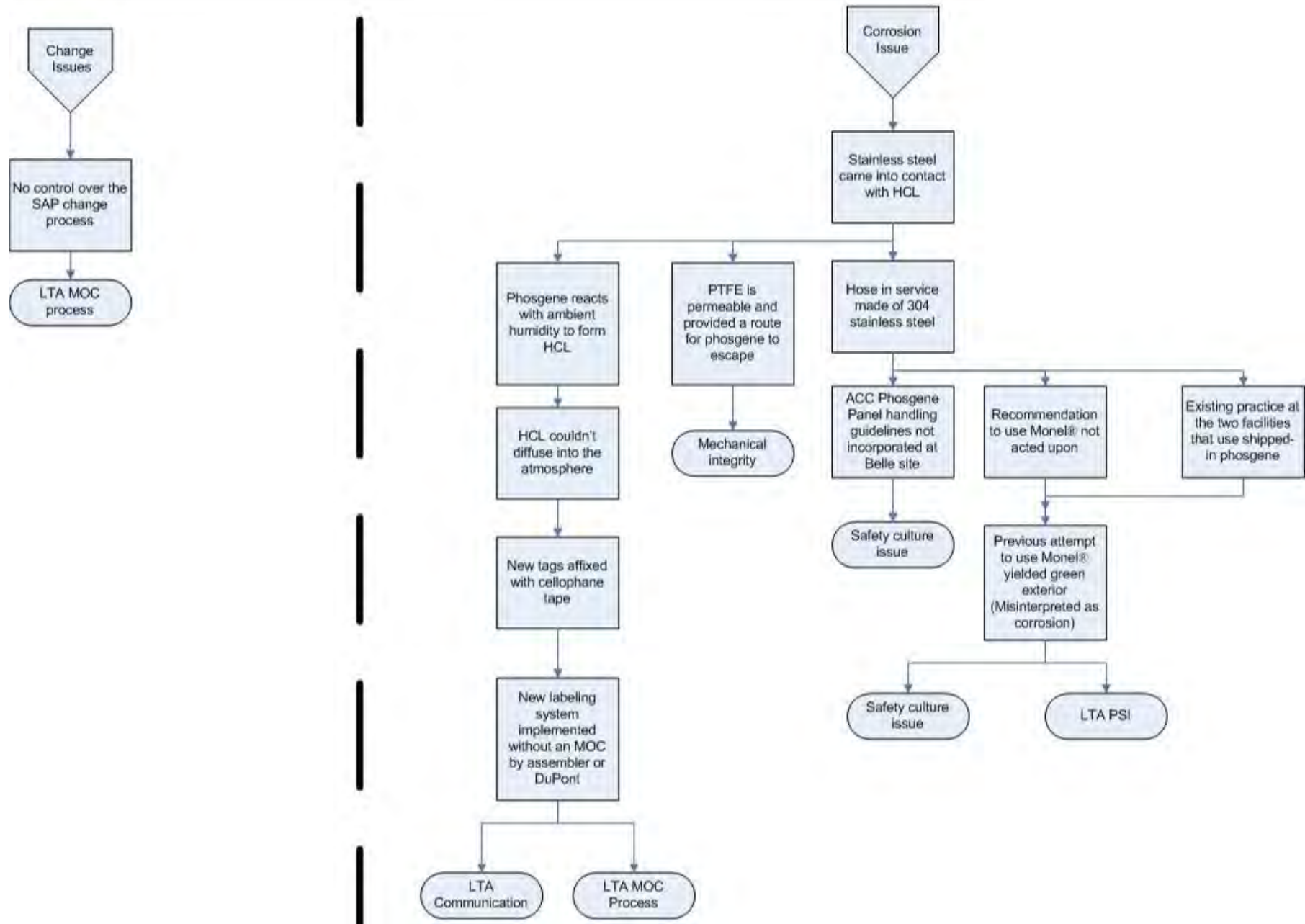
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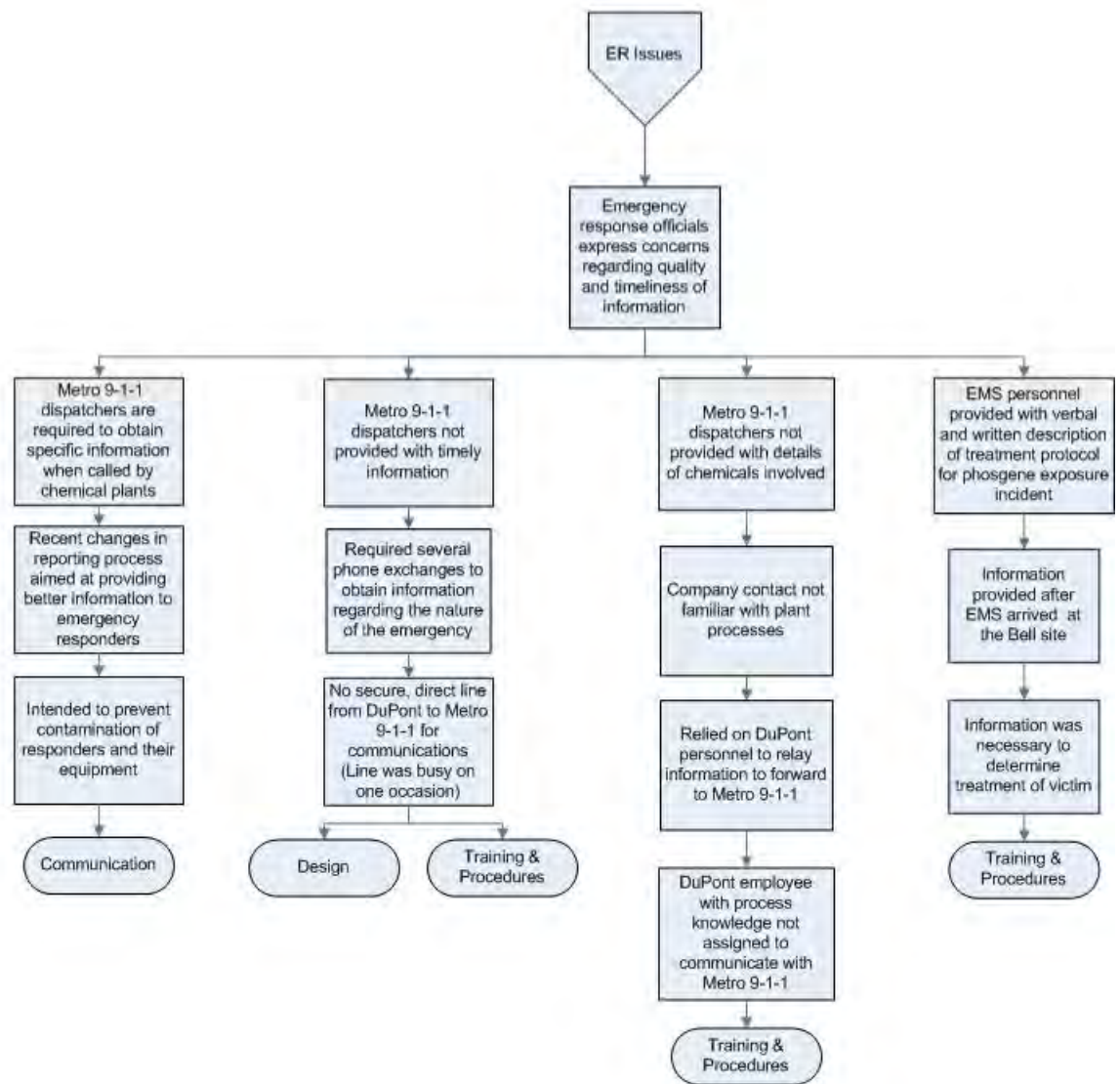
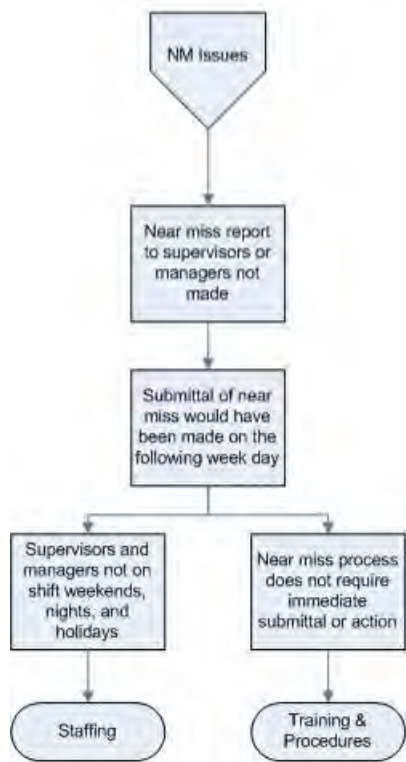
## Appendix A: Three Event Logic Tree



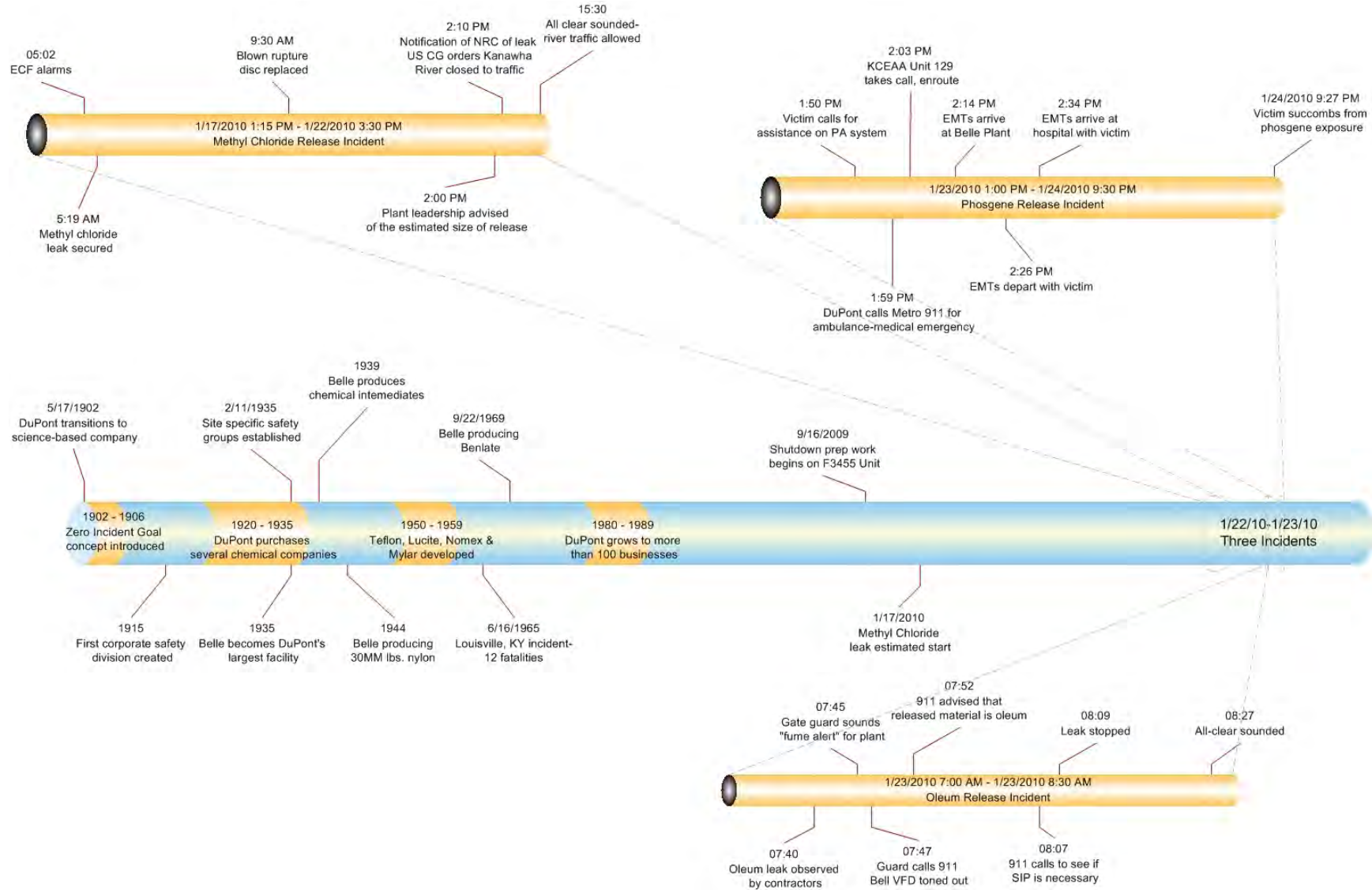








## Appendix B: Historical and Event Timeline





## Appendix C: SAP Program

The DuPont Belle Plant uses the SAP R/3 Plant Maintenance module to schedule preventive maintenance (PM) and repair work and track maintenance costs. Many companies use a Computerized Maintenance Management System (CMMS) such as SAP Plant Maintenance for this purpose. In particular, companies use the CMMS to schedule PM to ensure that PSM-critical equipment will function properly. This appendix gives additional detail on scheduling and completing PM jobs in SAP, and why SAP failed to issue work orders to change the hoses.

PM keeps plant equipment functioning properly, and to minimize the likelihood of a phosgene hose corroding and rupturing, DuPont created a PM job in SAP to replace the hoses regularly. The SAP Plant Maintenance module automatically schedules the job at the frequency DuPont designates.

In the SAP Plant Maintenance module, DuPont created an equipment number for the physical equipment and an electronic document, or “maintenance plan,” to store all information about the job. The maintenance plan is a complex form with many fields. One field, “confirmation required,” can be clicked “on” or “off.” If this button is “off,” SAP schedules the first hose change job; waits the specified time indicated in the interval field, such as “30 days”; and then automatically schedules another hose change job. Thus, when the button is “off,” by default SAP schedules hose change-outs “every 30 days,” which, for critical equipment subject to intermittent operation, is usually the desired option (CCPS, 1995). If the button is on, SAP requires that someone confirm that the hoses are changed. Thus, if the confirmation-required button is “on,” SAP schedules hose changes “30 days after the previous change,” but opens the possibility that no one will confirm the completion date in the system, creating a scenario where SAP will not schedule the hose change at the pre-determined interval.

Despite the computer-based and administrative controls that SAP and DuPont provided, in late 2006 someone changed the confirmation-required field for the phosgene hoses from "off" to "on"—or requiring confirmation. These administrative controls highlight gaps that contributed to the fatality.

When an SAP user account is created, access is provided according to the “work role” profile that DuPont establishes for the user. Only certain users would have had access to change the data in the maintenance plan for the phosgene hoses.

Programmers are “super users” who have higher level access than normal users and can write batch programs to change data, forms, and other SAP computer code that affects multiple pieces of equipment and multiple plant sites at once. As an administrative control at DuPont, programmers write computer code in a “development box” to prevent creating problems in the SAP “production box” that normal users see. When the programmer completes the code or downloads it to the “sandbox,” the process owners test the change to see that it performs as requested or if the change creates a problem. After the process owners approve the change, the programmer runs the code or downloads it to the “production box” and makes the actual change for regular users. These computer controls help ensure the integrity of the “production box” for regular users but were not enough to prevent the Belle Plant fatality.

The CSB discovered evidence relevant to the SAP change:

- The SAP work role controls allow programmers, process owners, and specific Belle Plant employees to access the phosgene hose maintenance plan.
- In 2005, the Belle Plant upgraded from SAP R/2 to the newer SAP R/3 partly because SAP R/3 included the new PM module. Converting from the previous CMMS to the SAP PM module was a large project that involved site personnel who verified the data in spreadsheets before contract SAP programmers uploaded the data into SAP.

Based on this evidence, the most likely scenario is that a programmer accidentally changed the confirmation-required field for the phosgene hoses. The change may have been an unintended effect of a valid change that DuPont requested or may have been an accidental change that went undetected.

## Appendix D: Phosgene Release Calculations

DuPont initially estimated that 0.7 pounds of phosgene released from the riverside cylinder hose and associated valving at the time of the rupture. After performing more detailed calculations, DuPont revised the estimated release quantity to 2.0 pounds of phosgene. The CSB performed calculations and modeled the release to verify the phosgene release quantity.

### Process Equipment

Figure 18 shows the hose and piping dimensions and the maximum amount of phosgene present in the piping system associated with the hose failure.

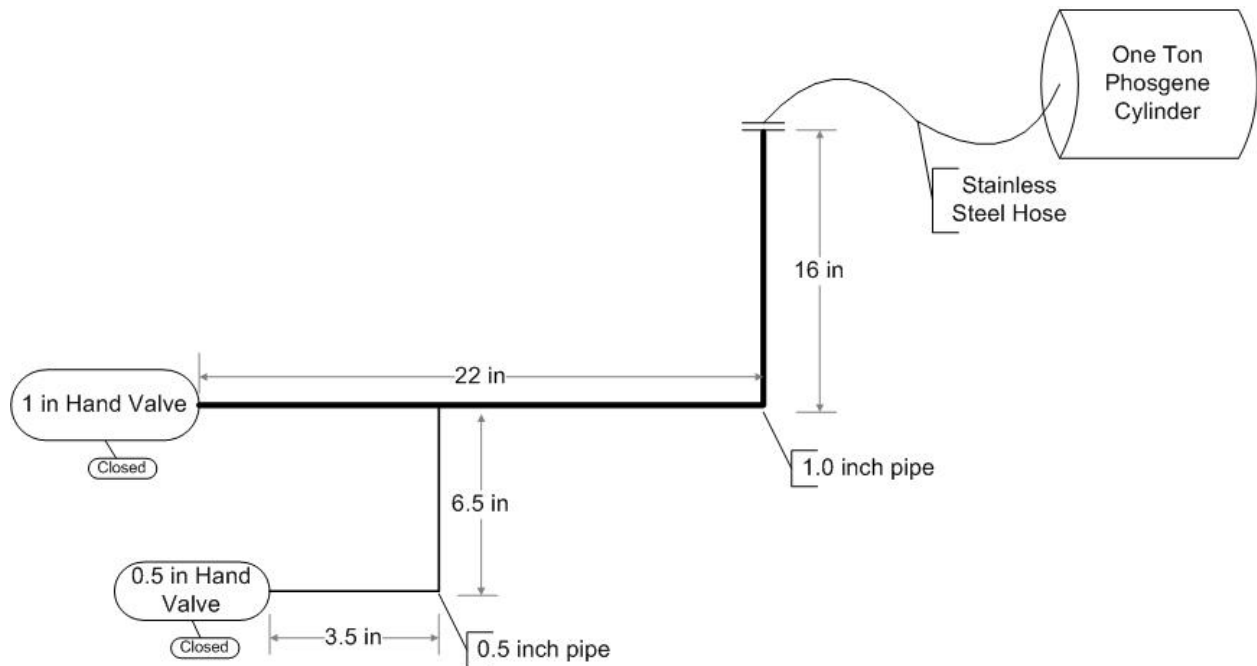


Figure 18. The hose and piping system that supplied phosgene for the release

- 1) Area of a circle:

$$\pi(r)^2 \quad \text{or} \quad \pi\left(\frac{D}{2}\right)^2 = (ft)^2 = ft^2$$

- 2) Volume of a cylinder is equal to the area of the circle, multiplied by the length ( $L$ ):

$$\pi\left(\frac{D}{2}\right)^2 * L = ft^2 * ft = ft^3$$

- 3) To determine weight, multiply by the density ( $\rho$ ):

$$\pi\left(\frac{D}{2}\right)^2 * L * \rho = ft^3 * \frac{lbs}{ft^3} = lbs$$

The density of phosgene, given that the ambient temperature was 8 °C:

$$\rho = 87.5 \frac{lb}{ft^3}$$

Phosgene contained in the 1-inch pipe:

$$D = 1.05 \text{ in} = 0.0875 \text{ ft}$$

$$L = 16 \text{ in} + 22 \text{ in} = 38 \text{ in} = 3.17 \text{ ft}$$

Thus,

$$\pi \left(\frac{D}{2}\right)^2 * L * \rho = \pi \left(\frac{0.0875}{2}\right)^2 * 3.17 * 87.5 = \mathbf{1.67 \text{ lbs}}$$

---

Phosgene contained in the 0.5-inch pipe:

$$D = 0.622 \text{ in} = 0.052 \text{ ft}$$

$$L = 6.5 \text{ in} + 3.5 \text{ in} = 10 \text{ in} = 0.83 \text{ ft}$$

Thus,

$$\pi \left(\frac{D}{2}\right)^2 * L * \rho = \pi \left(\frac{0.052}{2}\right)^2 * .83 * 87.5 = \mathbf{0.154 \text{ lbs}}$$

---

Phosgene contained in the 0.5-inch valve:

$$D = 0.622 \text{ in} = 0.052 \text{ ft}$$

$$L = 5.5/3 = 1.83 \text{ in} \text{ (1/3 the full length of the valve, since it was closed)}$$

$$1.83 \text{ in} = 0.153 \text{ ft}$$

Thus,

$$\pi \left(\frac{D}{2}\right)^2 * L * \rho = \pi \left(\frac{0.052}{2}\right)^2 * .153 * 87.5 = \mathbf{0.028 \text{ lbs}}$$

---

Phosgene contained in the 1-inch valve:

$$D = 1.05 \text{ in} = 0.0875 \text{ ft}$$

$$L = 6.5/3 = 2.17 \text{ in} \text{ (1/3 the full length of the valve, since it was closed)}$$

$$2.17 \text{ in} = 0.181 \text{ ft}$$

Thus,

$$\pi \left(\frac{D}{2}\right)^2 * L * \rho = \pi \left(\frac{0.0875}{2}\right)^2 * .181 * 87.5 = \mathbf{0.095 \text{ lbs}}$$

---

Phosgene contained in the quarter inch, four foot long hose:

$$D = 0.25 \text{ in} = 0.021 \text{ ft}$$

$$L = 48 \text{ in} = 4 \text{ ft}$$

Thus,

$$\pi \left(\frac{D}{2}\right)^2 * L * \rho = \pi \left(\frac{0.021}{2}\right)^2 * 4 * 87.5 = \mathbf{0.12 \text{ lbs}}$$

---

The sum of phosgene in the system:

$$1.67 + 0.154 + 0.028 + 0.095 + 0.12 = \mathbf{2.067 \text{ lbs of phosgene released}}$$

## Phosgene Dose Calculation

Using the phosgene release quantity above, the CSB calculated the approximate concentration of phosgene the fatally injured operator was exposed to. Assuming the operator was three feet away from the release, and the phosgene instantly vaporized in a spherical fashion from the point of release, the operator would have received a lethal dose of phosgene in less than a tenth of a second. This calculation will assume homogeneous concentration/mixing within the spherical phosgene gas cloud.

$$\text{Air molecular weight} = 28.97 \frac{\text{g}}{\text{mol}^{62}}$$

$$\text{Phosgene molecular weight} = 98.9161 \frac{\text{g}}{\text{mol}}$$

$$\text{Volume of a sphere with a 3 ft radius} = \frac{4}{3} * \pi * (3)^3 = 113.1 \text{ ft}^3$$

$$2.067 \text{ lbs phosgene} * \frac{453.593 \text{ g phosgene}}{1 \text{ lb phosgene}} * \frac{1 \text{ mol phosgene gas}}{98.9161 \text{ g phosgene}} * \frac{22.414 \text{ L phosgene gas}^{63}}{1 \text{ mol phosgene gas}} * \frac{1 \text{ ft}^3 \text{ phosgene gas}}{28.3168 \text{ L phosgene gas}} = 7.5 \text{ ft}^3 \text{ phosgene gas}$$

$$\text{Phosgene concentration in the sphere (uniform dispersion)} = \frac{7.5 \text{ ft}^3}{113.0973 \text{ ft}^3} = .0661 \text{ or } 6.61 \text{ volume\% phosgene; effectively} = 6.63 \text{ mol\% phosgene}$$

$$\begin{aligned} &\text{Average total molecular weight of gas (phosgene - air mix)} \\ &= \left( \left( 98.9161 \frac{\text{g}}{\text{mol}} \text{ phosgene} * 6.63\% \right) + \left( 28.97 \frac{\text{g}}{\text{mol}} \text{ air} * (100\% - 6.63\%) \right) \right) \\ &= 33.6 \frac{\text{g}}{\text{mol}} \text{ gas in the sphere} \end{aligned}$$

$$\begin{aligned} \text{Weight percent of phosgene} &= 6.63 \text{ mol\% phosgene} * \frac{98.9161 \text{ g phosgene}}{1 \text{ mol phosgene}} * \frac{1 \text{ mol gas}}{33.6 \text{ g gas}} \\ &= 0.195 \text{ or } 19.5 \text{ wt\% phosgene in the sphere or } 195,000 \text{ ppm} \end{aligned}$$

$$\begin{aligned} \text{Where a lethal dose is estimated to be } 300 \text{ ppm} * \text{min (Collins et al, 2011)} &= \frac{300(\text{ppm} * \text{min})}{195,000 \text{ ppm}} \\ * \frac{60 \text{ seconds}}{1 \text{ minute}} &= 0.09 \text{ seconds to receive a lethal dose of phosgene} \end{aligned}$$

<sup>62</sup> A mole (mol) of any substance has a mass (g) exactly equal to that substance's molecular mass. Mol is a base unit in the International System of Units for the amount of substance.

<sup>63</sup> Ideal gas law.

## Vapor Cloud Dispersion Modeling

The CSB used the ALOHA<sup>®</sup> (Area Locations of Hazardous Atmospheres) 5.4.1 program to model the phosgene release based on the characteristics of the release and atmospheric conditions on the afternoon of January 23, 2010. The National Oceanic and Atmospheric Administration (NOAA) and the U.S. EPA developed ALOHA to estimate the threat zones associated with hazardous chemical releases from toxic plumes, fires, and explosions. The user inputs chemical property and weather information and the program generates a user-defined release scenario that shows the concentration of toxic gases within a radius of the release source.

The following assumptions were used to model the phosgene release in ALOHA:

Atmospheric and Environmental Conditions:

Atmospheric temperature: 50°F

Wind speed: calm, 1.5 m/s

Wind direction: from the north

Humidity: 66%

Cloud cover: scattered

Surrounding terrain: urban

### Release conditions

Chemical: Phosgene

Amount released: 2 pounds

Release type: instantaneous

Height of release: 4 feet

The ALOHA program generated a display of concentration “threat zones” over a distance downwind from the source of the release. Using the U.S. EPA MARPLOT program, threat zones are displayed over a satellite map of the area using a graphical information system (GIS) interface (Figure 19).



Figure 19. ALOHA estimate of phosgene concentrations with MARPLOT GIS overlay

The ALOHA program estimated threat-zones for three user selected phosgene concentrations:

- 2 ppm (IDLH), 0.2 miles from release source
- 0.5 ppm (odor threshold and phosgene alarm set point), 0.3 miles from release source
- 0.2 ppm (ERPG-2<sup>64</sup>), 0.4miles from release source

---

<sup>64</sup> ERPG-2 is the concentration to which all could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action (AIHA, 2008).



The release estimates from the ALOHA program are based on the weather conditions recorded at the Charleston Yeager Airport around the time of the January 23, 2010 phosgene release, but may not accurately represent atmospheric conditions at the plant. The ALOHA program also does not consider the topography or terrain surrounding the plant. The fence line monitors south and southwest of the phosgene shed recorded phosgene concentrations between 0 and 0.27 ppm, suggesting phosgene vapor may have traveled south of the DuPont Belle plant fence line toward the river. The ALOHA threat-zone overlay in Figure 19 displays a model of the worst case release conditions indicating IDLH concentrations of phosgene could have been present on the Kanawha River shortly after the release and lower concentrations could have traveled across the river. There were no reports of odors or exposure symptoms from the community on the afternoon of the phosgene release incident.

## **Appendix E: Hazard Analysis for Phosgene Use at Belle**

*(Documents in this appendix are redacted for confidentiality by black and white out)*

### **List of Acronyms, Abbreviations and Terminology**

dia	diameter
flashing	instantly vaporizing liquid
IHI	Individual Hazard Index
LD50	50% lethal dose
MM	million (old notation style)
PHI	Process Hazard Index
ppm	parts per million

AG-6 REV. 4/86



E. I. DU PONT DE NEMOURS & COMPANY  
INCORPORATED  
BELLE, WEST VIRGINIA 25015

CC:



AGRICULTURAL PRODUCTS DEPARTMENT  
BELLE PLANT, 901 W. DU PONT AVENUE

June 2, 1988

CONFIDENTIAL

[REDACTED]  
AGRICULTURAL PRODUCTS DEPARTMENT  
[REDACTED]  
WILMINGTON

BELLE PHOSGENE PLANT  
PRELIMINARY RISK ASSESSMENT

- References: (1) Attached Memo, [REDACTED] to [REDACTED], "BELLE PHOSGENE PLANT PRELIMINARY RISK ASSESSMENT REVISED CALCULATIONS", Dated May 19, 1988
- (2) Attached Memo, [REDACTED] to [REDACTED], "IS THE PHI A GOOD RISK PARAMETER?", Dated April 29, 1988
- (3) Attached Memo, [REDACTED] to [REDACTED], "DU PONT RISK CRITERIA", Dated May 6, 1988

Reference 1 describes risk assessment studies pertaining to the existing and proposed phosgene supply operations at the Belle Plant. References 2 and 3 question the value of PHI as a means of directing resources towards cost effective improvements in safety.

We plan to continue to work with [REDACTED] towards reducing the uncertainties in the Belle phosgene risk assessment studies preparatory to arriving at a decision concerning a ventilated enclosure for the Belle phosgene plant. We anticipate a decision on this matter when the current appraisal cost estimates are available three months after authorization of the Engineering Department P&E.

Please advise the writer if you have comments or suggestions.



EN-1028 REV 11-86



E. I. DU PONT DE NEMOURS & COMPANY  
INCORPORATED  
P. O. Box 6090  
NEWARK, DE 19714-6090

CC: [REDACTED]

ENGINEERING DEPARTMENT  
LOUVIERS BUILDING

May 19, 1988

[REDACTED]  
AGRICULTURAL DEPT  
BELLE PLANT

BELLE PHOSGENE PLANT PRELIMINARY RISK ASSESSMENT  
REVISED CALCULATIONS

#### INTRODUCTION

A previous assessment transmitted as E-mail dated March 22, 1988, was discussed at Belle Plant on March 29 and revisions suggested. This note documents the results of those revisions.

The four cases considered are:

1. Operating with a liquid phosgene feed from cylinder to No. 2 reactor.
2. Vaporizing the feed from the cylinders.
3. Installing a plant to make phosgene from CO and Cl<sub>2</sub>.
4. Enclosing the phosgene plant.

#### EXPLANATION OF TABLES

One change to all the assessments was the use of 720 ppm minutes as an LD50 instead of the 2700 ppm minutes used previously.

#### Table 1

##### Item 1

400 ft of 2 in. pipe, containing 800 lbs phosgene. Large leak interval is 1,200 years for 300 ft pipe (see letter [REDACTED] to [REDACTED] 5/13/87).

2

May 19, 1988

The line is pressurized to 60 psig to feed the reactor for 30% of the time and the remainder of the time it is assumed to be at phosgene vapor pressure of 8.7 psig.

Assuming flashing flow gives 70 & 22.4 lbs/min for pressurized and non-pressurized flow respectively from a 0.4" equivalent diameter hole.

Item 2

UK data, no failures in 200,000 cylinder years is equivalent to a failure interval of 600 K years. Arbitrary failure 0.5" diameter, flashing flow from pressurized cylinder.

Item 3

Assumed stored cylinders on rollers so that first 20 minutes leak assumed in liquid (flashing) then cylinder rolled to leak vapor for 15 minutes then capped.

Item 4

Pigtails made and broken 500 times per year. One in 10,000 not done correctly, one in 10 not capable of being corrected by man on the spot. Assume someone will close cylinder valve within 10 minutes. Flashing flow from full bore pigtail 0.194" hole.

Item 5

The American Trucking Association reports that the 1985 average for reportable accidents involving carrier trucks is 1.3 accidents per MM miles. Statistics from DE, MA, NJ, NY, and PA indicate that the overall accident rate for all vehicles is 3.05 accidents per MM miles. US Highway Statistics Division, Office of Highway Planning, 1984 gives the fatality rate as 2.58 fatalities per 100 MM miles. Assuming the number of fatalities per accident is the same for trucks as for all vehicles one might deduce there would be

1.1 (= 2.58 x 1.3 + 3.05) fatalities per 10 MM truck miles

Table 2

Item 1

As Table 1, Item 1, except vapor flow.

Also assumed vaporizer level would fall quickly until the maximum flow is controlled by the liquid flow control valve (usually set at 7 lbs/min.

3  
May 19, 1988  
[REDACTED]

Item 2,3,4,5

As Table 1, Item 2, 3, 4, and 5.

Item 6

The vaporizer is assumed to hold 25 lbs when operating (30% of time) and about 12 lbs the remainder of the time. Again a leak would deinventory the vaporizer and then the flow would be limited to 7 lbs/min by the flow control valve.

The failure data transmitted from [REDACTED] to [REDACTED] by E-mail, July 31, 1987-August 5, 1987, suggests a failure interval for vaporizer of 180 years. The works suggest only one serious failure is relevant in phosgene service giving a 540 year failure interval equivalent to 1,800 years in operation and 770 in standby. Flow rates (flashing) through a 0.5" hole would be 109 lbs per min for 1/4 min followed by 7 lbs/min for 3/4 minutes until phosgene detectors isolated feed, and in standby 109 lbs for 0.1 minutes.

Table 3

Item 1

Assume catastrophic release from storage tank. Small leaks will have little impact.

Item 2

The works consider hose rupture due to tank truck driving off as incredible because of carefully enforced administrative procedures. Since this type of incident does happen, the works would have to convince the outside world that with their procedures this failure is incredible.

Item 3

Using same failure rates as Table 1, Item 1, assumed 100 psig, 0.4" diameter hole, 30 minutes to detect and isolate.

Item 4

1.1 fatalities per 100 MM miles.

Item 5

Similar to Table 1, Item 2, but assumed all chlorine is at 100 psig since chlorine vapor pressure at 20°C is 85 psig.

4

May 19, 1988  
[REDACTED]

Item 6

Similar to Table 2, Item 6, except two failures per 540 years are relevant for chlorine.

Item 7

Similar to Table 1, Item 4.

Item 8

1.1 fatalities per 100 MM miles.

Item 9

Used same failure rate for phosgene process as for phosgene vaporizer (Table 2, Item 6). However, the leak rate is determined by the production rate which is at 5 MM lbs/yr is about 10 lbs/min. We have arbitrarily assumed it would take 10 minutes to isolate the leak and therefore the volume in the process is irrelevant.

In standby mode we assume, probably pessimistically, that 10 lbs phosgene could be released.

Item 10

A more direct route would use 200 ft pipe. Production rate would again limit leak rate assumed operating only 30% of time.

Table 4

As Case 3 except items 5, 6, 7 and 9 would be enclosed. I have assumed the ventilation and scrubbing system would have a one in 1,000 chance of failing.

CONCLUSIONS

- o The uncertainties in data are enormous.
- o The gas dispersion model is not valid for under about 100 meters which covers most of the on-site analysis.
- o Case 3 meets Du Pont guidelines for on-site and off-site IHIs.
- o There is no Du Pont guideline for off-site PHI.
- o See notes sent to [REDACTED] (5/17/88) re on-site PHI criteria

5

May 19, 1988

[REDACTED]

(the PHI of 10,000 is a guideline target, not a mandatory specification).

- o Case 4 does not meet the PHI target of 10,000.
- o Spending \$2 MM for an enclosure to get from Case 3 to Case 4 saves 14.4 lives per 10,000 years. (Almost all the improvement is in on-site risk. Off-site risk improvement is not significant.) This sets a value of life plus public outrage at \$143 MM.
- o It may be that in the present circumstances the business can afford \$2 MM for an enclosure; however, in the long run can we afford to take such action which has such a small impact on safety and yet sets a precedent for all highly toxic material activities.

ENGINEERING SERVICE DIVISION  
Air Quality and Hazards Evaluation

[REDACTED]

[REDACTED]



TABLE 1  
 Liquid Phosgene Feed to No. 2 Reactor

Item	Leak	Failure Interval	Failures Per 10,000 Years	Leak Rate Lb/Min	Dur Mins	Onsite		Offsite		Max Probable Risk	IHI
						Fats Per 10,000 Yr	Inc	Fats Per 10,000	Per Inc		
1 400'x2" pipe contains 800 lbs phosgene	0.4"dia hole at 60psig for 30% time	3000 (1200x3x100) 4 30%	3.3	70	12	23.7	78.2	2.4	7.9	.56	0.29
	As above except at 8.7psig for 70% time	1286	7.8	22.4	36	5.6	43.7	.31	2.4	.41	0.047
2 1x1 ton cylinder	Say 0.5" hole	600M	0.017	109	10	34.9	0.59	4.3	0.073	.11	0.0021
3 9x1 ton cylinder	Say 0.5" hole	67000	0.15	35	20	9.2	1.4	0.6	0.09	.48	0.0038
				8.3	15	.83	0.12	0	0	.16	0
4 Pigtails	Break 0.194"	200	50	16	10	2.0	100	.0009	0.045	.33	0.0017
5 Road transport 53,000 miles/yr									(5.8)		
Totals							224		10.5	24.6	0.34

(PHI = 45)

TABLE 2  
 Vaporized Phosgene Feed

Item	Leak	Failure Interval	Failures Per 10,000 Years	Leak Rate Lb/Min	Dur Mins	Onsite		Offsite		Max Probable Risk Onsite	Max Probable Risk Offsite	IHI Onsite	IHI Offsite
						Fats Per 10,000 Yr	Fats Per 10,000 Inc	Fats Per 10,000 Yr	Fats Per 10,000 Inc				
1 400' x 2" pipe vapor filled 30% time 13 lbs	Blown gasket 0.4" dia at 60psig	3000	3.3	18.4 7	2 8	.75 .57	2.5 1.9	0 0	0 0	.15 .11	0 0	0.57 0.42	0 0
2 1x1 ton cylinder	Say 0.5" hole	600M	0.017	109	10	34.9	0.59	4.3	0.073	.59	.11	0.011	0.0021
3 9 x 1 ton cylinder	Say 0.5" hole	67000	0.15	35 8.3	20 15	9.2 .83	1.38 0.12	0.6 0	0.09 0	.48 .16	.022 0	0.082 0.027	0.0038 0
4 Pigtail	Break 0.194	200	50	16	10	2.0	100.0	0.0009	0.045	.33	.00003	18.8	0.0017
5 Road 53000 mile per year													(5.8)
6 (a) vaporizer 25 lbs online	Unknown Say 0.5"	1800	6	109 7	1/4 3/4	2.5 .0087	15 0.052	.00045 0	0.0027 0	.45 .0017	.000017 0	3.1 0.12	0.00012 0
(b) offline Say 12 lbs	Unknown Say 0.5"	770	13	109	0.1	2.5	32.5	.00045	0.0059	.45	.000017	6.7	0.00025
Total							154		0.22			29.8	0.008

(PHI = 65)

TABLE 3  
 New Phosgene Plant

Item	Leak	Failure Interval	Leak Rate Lb/Min	Dur Mins	Failures Per 10,000 Years		Onsite		Offsite		Max Probable Risk	IHI	
					Fats Per 10,000 Yr Inc	Fats Per 10,000 Yr Inc	Fats Per 10,000 Yr Inc	Fats Per 10,000 Yr Inc	Onsite	Offsite			
<u>C0</u> 1 CO storage tank	Catastrophic	100M	40000	puff	2.9	0.29	0.04	0.004	0.004	0.47	.0017	0.054	0.00019
2 6 truck shipments per year	Unloading hose rupture due tank truck driving off whilst connected considered by plant to be not a credible event. The administrative controls must convince others of this.												
3 2000 ft 2" vapor line	0.4" hole	180	15	30	$8 \times 10^{-6}$	0.0004	0	0	0	$.16 \times 10^{-5}$	0	0.0001	0
4 10000 truck miles per year													
													(1.1)
<u>C1</u> 5 (a) 1x1 ton cylinder	0.5" dia hole	600M	150	8	1.6	0.026	0.0088	0.00014	0.0088	0.27	.00031	0.0049	$5.7^{-7}$
(b) 7x1 ton cylinder	0.5" dia hole	86M	37	15	0.085	0.01	0	0	0	.016	0	0.0022	0
6 (a) Vaporized Online	0.5" dia hole	900	150	1/4	0.18	1.98	0	0	0	.035	0	0.44	0
(b) Offline	0.5" dia hole	390	10	3/4	$3.4 \times 10^{-9}$	0	0	0	0	neg	0	0	0
7 Pigtails	.194" dia	200	23	10	0.016	0.8	0	0	0	.003	0	0.17	0

Item	Leak	Failure Interval	Failures Per 10,000 Years	Leak Rate Lb/Min	Dur Mins	Onsite		Offsite		Max Probable Risk	IHI		
						Fats Per 10,000 Yr Inc	Fats Per 10,000 Inc	Onsite	Offsite		Onsite	Offsite	
8 11250 truck miles per year													
(1.2)													
CO CL <sub>2</sub>													
9 (a) Process Online	0.5" dia	1800	6	10	10	1.1	6.6	0	0	.21	0	1.44	0
(b) Standby	0.5" dia	770	13	10	1	.038	0.49	0	0	.0073	0	0.11	0
10 200' x 2"	0.4" dia	6000	1.7	10	10	1.1	1.9	0	0	.21	0	0.37	0
Totals							16.7					3.6	.00031

(PHI = 600)

TABLE 4  
 Enclosed Phosgene Plant

Item	Leak	Failure Interval	Failures Per 10,000 Years	Leak Rate Lb/Min	Dur Mins	Onsite		Offsite		Max Probable Risk	IHI	
						Fats Per 10,000 Yr	Fats Per Inc	Fats Per 10,000	Fats Per 10,000			
						puff					Onsite	Offsite
<u>CO</u>												
1 CO storage tank not enclosed	calastrophic	100M	0.1	40000		2.9	0.29	.04	0.004	0.47	.054	.00019
2 6 truck shipments not enclosed	Not a credible incident - see Table 3, Item 2											
3 2000' x 2" pipe vapor not enclosed	.4" dia	180	56	15	30	$8 \times 10^{-6}$	0.0004	0	0	$0.16 \times 10^{-5}$	.0001	0
4 10000 truck miles per year									(1.1)			
<u>CL2</u>												
5 (a) 1 x 1 ton cylinder enclosed	.5" dia hole	600MM	0.000016	150	8	1.6	.000026	0.0088	$10^{-7}$	0.27	$4.9^{-6}$	$5.7^{-9}$
(b) 2 x 1 ton cylinder enclosed	.5" dia hole	300MM	0.000032	150	10	1.8	.000058	0.025	$8 \times 10^{-7}$	0.27	$9.9^{-6}$	$3.1^{-8}$
(c) 5 x 1 ton cylinder not enclosed	.5" dia hole	120M	0.083	37	15	.085	.000003	0	0	.016	$5.8^{-7}$	0
				150	10	1.8	.15	0.025	0.002	0.27	.00086	0.026
				37	15	.085	.007	0	0	.016	0.0015	0
6 (a) Vaporized Online enclosed	.5" dia hole	900M	0.011	150	1/4	0.18	.002	0	0	.035	0.00044	0
(b) Offline enclosed	.5" dia hole	390M	0.026	10	3/4	$3.4 \times 10^{-9}$	0	0	0	neg	0	0
				150	0.1	0.18	0.005	0	0	0.35	0.0010	0

TABLE 4  
 (CONTINUED)

Item	Leak	Failure Interval	Failures Per 10,000 Years	Leak Rate Lb/Min	Dur Mins	Onsite		Offsite		Max Probable Risk		IHI Onsite	IHI Offsite
						Fats Per 10,000 Yr Inc	Fats Per 10,000 Inc	Fats Per 10,000 Yr Inc	Fats Per 10,000 Inc	Onsite	Offsite		
7 Pigtailes enclosed	.194"	200M	0.05	23	10	0.016	0.0008	0	0	.003	0	0.00017	0
8 11250 truck miles per year													
9 (a) Process	0.5" dia	1800M	0.006	10	10	1.1	.00066	0	0	.21	0	0.0014	0
9 (b) Standby	0.5" dia	770M	0.013	10	1	.038	.00049	0	0	.0073	0	0.00011	0
10 200' x 2"	.4"	6000	1.7	10	10	1.1	1.9	0	0	.21	0	0.37	0
					Total		2.3					.40	0.00027

(1.2)

(PHI = 4350)

TABLE 5  
 SUMMARY

<u>Totals</u>	<u>On Site</u>			<u>Off Site</u>		
	<u>Fats per</u> <u>10,000 yrs</u>	<u>PHI</u>	<u>IHI</u>	<u>Fats per</u> <u>10,000 yrs</u>	<u>Transport</u> <u>Fats per</u> <u>10,000 yrs</u>	<u>IHI</u>
Case 1	244	45	24.6	10.5	5.8	0.34
Case 2	154	65	29.8	0.22	5.8	0.008
Case 3	16.7	600	3.6	0.007	2.3	0.00031
Case 4	2.3	4350	0.4	0.006	2.3	0.00027

ENCLOSURE



E. I. DU PONT DE NEMOURS & COMPANY  
INCORPORATED

P. O. Box 6090  
NEWARK, DE 19714-6090

ENGINEERING DEPARTMENT  
LOUVIERS BUILDING

April 29, 1988



IS THE PHI A GOOD RISK PARAMETER?

The attached note challenges the use of PHI as a good parameter for risk criteria.

It is a note I have been intending to write for years because we and other companies have been spending inefficiently on reducing process hazards.

However, after a visit to a General Electric phosgene plant near Mount Vernon early in April, I recognized that this inefficiency had reached a peak with precedent setting action GE had taken to enclose, purge, and scrub the plant.

If we accept the premise that we spend money on process hazards to save lives, prevent damage and avoid public outrage, and if we use the number of lives saved as a measure of these three contributions, then the \$40MM GE spent to enclose their plant to achieve an arbitrarily established FN curve criterion (a sort of sophisticated PHI) represents a spending rate of about \$4 billion per life saved.

Such a precedent is neither in the interests of GE, Du Pont, the chemical industry, nor the public as a whole. But using criteria like FN curves, PHIs, and IHIs without also considering the cost/risk/benefit tradeoff explicitly will inevitably lead to increasingly inefficient use of resources.

ENGINEERING SERVICE DIVISION  
Air Quality and Hazards Evaluation





DU PONT RISK CRITERIA

There is no such thing as an acceptable risk per se. A risk is only acceptable "in the circumstances".

In many cases, a risk is acceptable to a person because of the benefit he derives from taking the risk, whether that benefit is financial, health or pleasure.

Whenever the benefits accrue to the person taking a risk, a fair tradeoff can be negotiated in the circumstances and an "acceptable risk" level can be determined. Such tradeoffs are common between companies and employees where the risks are explained, training and protection are provided and the employee benefits with a good job.

However, each case will be different; the circumstances will include a variety of factors, but one of the most important and variable will be the cost of reducing the risk.

The idea of establishing uniform criteria for in-plant risk levels in Du Pont was to provide consistency across the company, but consistent risk levels do not lead to the most efficient use of resources. There are situations where rigid adherence to such criteria leads to wasteful use of resources, and as we try to improve our standards, these situations will occur more frequently.

We are not spending money and resources to reduce risk to some arbitrarily chosen level; we are spending that money to save lives, damage to one's reputation, property, the environment and to avoid public outage.

So, if we use lives as a measure of all the adverse damage, it should be incontrovertible that we ought to save the maximum number of lives for any money we spend.

Let us consider an example; to illustrate the point.

Let us assume that in this example, all the other damages etc. are proportional to the loss of life, so we shall just be considering the lives lost.

Consider five processes as follows:

Process	Existing PHI	Existing Fats/ 10,000 Yrs	Cost to Improve PHI to 10,000	No. of Fats Per 10,000 Yrs If PHI=10,000	Cost to Improve PHI to 100,000
1	5,000	2	\$ 10,000	1	\$50,000
2	5,000	2	\$100,000	1	\$1MM
3	5,000	2	\$ 10,000	1	\$50,000
4	Not Known	?	?	?	?
5	Not Known	?	?	?	?

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 April 26, 1988

Plant Manager A rigidly adheres to the guideline and spends \$120M getting processes 1, 2, and 3 to the PHI guideline of 10,000. In so doing, he saves three lives per 10,000 years. Assuming a 10-year plant life, he is saving 0.025 lives per \$1MM spent.

Plant manager B decides to spend his \$120M improving plants 1 and 3 to 100,000 and leaving plant 2 alone. He saves 3.8 lives per 10,000 years -- equivalent to saving 0.032 lives per \$1MM spent.

Plant Manager C decides to spend \$20,000 on improving Plants 1 and 3 to 10,000 PHI and does a risk assessment on Plants 4 and 5, yielding the following information:

Process	Existing PHI	Existing Fats/ 10,000 Yrs	Cost to Improve PHI to 6,000	Improved Fats per 10,000 Yrs	Cost to Improve PHI to 10,000
4	3,000	3.33	\$50,000	1.67	\$200,000
5	3,000	3.33	\$50,000	1.67	\$200,000

Plant Manager C now decided to spend an additional \$100M improving 4 and 5 to 6,000 PHI, saving 3.33 lives.

Plant Manager C has, in Step 1, saved 0.1 lives per \$1MM; in Step 2 saved 0.0333 lives per \$1MM; and in Steps 1 and 2 combined, saved 0.044 lives per \$1MM.

Summarizing, we have:

Plant Manager	Spent	Saving Lives Per 10,000 Yrs	At Lives/\$M	No. of Plants Achieving Target PHI of 10,000
A	\$120M	3	0.025	3
B	\$120M	3.8	0.032	2
C	\$120M	5.3	0.044	2

Who is working in the best interests of Du Pont; it's employees, it's reputation, etc?

The numbers used are not from examples nor are they intended to indicate appropriate levels of spending. However, no matter what numbers are used, they will always illustrate that evaluating the benefits (lives saved, in this case) per \$ spent will always define the most cost-effective use of resources.

Conclusion

Seeking to achieve an arbitrary PHI regardless of cost is not the way to use numerical risk assessment nor the most cost-effective way to spend

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April 26, 1988

money to improve risk. If we insist on using the PHI as our major criterion then we should be content if we can match the PHI target for reasonable cost, but if there are circumstances where the cost of achieving the target appears to be too high we should use the lives saved per \$1MM to decide whether such expenditure is a wise use of resources.

Fortunately, we usually have little difficulty in achieving our PHI target of 10,000, even if we do spend our resources inconsistently in so doing. However, if there is ever a need to improve or add to our Company Guidelines, the use of PHI as a primary criterion should be rigorously challenged since the above illustrates only one of the problems associated with its use.

#### Risks to the Public

It is not the intention of this note to consider off-site risks. The problems associated with risk criteria for the public are compounded for a variety of reasons.

- o We never deal with the public (they stay at home, don't attend meetings, etc). The only ones we ever deal with are the special interest groups.
- o They see no benefit accruing from the risks of living near a chemical plant so the risk benefit tradeoff does not exist in their minds.
- o They do not understand FN curves, probabilities or even the simplest presentation of the numbers.
- o Their perception of the risk is what dominates their thinking (and their perception often is totally different from the actual risk).

The numerical criteria quoted in S&OH Guideline 6.7 therefore needs treating with ultimate caution.



MORE COMMENTS ON PHI CRITERIA

Whilst we all recognize that there is a need to revise our risk criteria, there is an even bigger need to explain how to use the existing ones.

The ignorance which abounds concerning PHI and IHI indicates that any revision should be towards simplification.

Whatever new criteria are chosen must be explained and publicized so that their meaning and application are clear and unambiguous. (What chance does the public stand of understanding the subject when the majority of Du Pont technical staff can't.)

The PHI was introduced solely to deal with the multiple fatality cases; if we could guarantee that all our incidents involved no more than one or two persons (and our history shows this is pretty close to the truth) the IHI criterion would have been sufficient and we would never have needed the PHI criterion.

The PHI criterion of 10,000 years was introduced for one risk, say \$1- or- \$2MM, and not for the whole plant site.

Extrapolating to large plants and smaller PHIs is not only unnecessary if all the incidents are involving one one or two casualties, but can also be quite inconsistent. To illustrate my point, consider three plants (A, B, and C) each with 10 processes as follows:

Plant A has 10 risks each with an IBI = 10,000. Each risk therefore has a PHI of 10,000 and with one operator at risk each operator would have an IHI = 1.1.

Plant B has one risk with an IBI = 1,000 giving a PHI of 1,000, one operator at risk with an IHI = 11 and the remaining nine plants having no risk.

Plant C has one risk with an IBI = 10,000 but with 10 operators affected by each incident gives a PHI of 1,000. Each operator's risk is an IHI of 1.1. The remaining nine plants have no risk.

All three plants have a total PHI of 1,000 which might be said to meet the extrapolated PHI target for a large area of risk. All three plants kill 10 people over 10,000 years.

The following comments are suggested by the example:

Summing risks over a large site does not help to improve safety nor give any clearer impression of the risks. In fact, it clouds the issue (all three plants appear, in total, to be acceptable).

Summing PHIs confuses the issue the PHI was introduced to deal with, namely the large incident, the risk in Plant C, putting 10 operators at risk, isn't highlighted by the PHIs in the example.

The use of the PHI doesn't do anything to ensure each operator has his fair share of risk (one Plant B operator has an IHI = 11).

The use of the total PHI would suggest no effort (or equal effort) is required on each plant.

The use of individual PHIs would suggest no effort on Plant A, probably weight more effort towards Plant C because of the larger incident.

The use of the IHI would suggest no effort on Plant A and probably weight more effort towards Plant B because of the higher IHI.

The use of a cost per life criterion would put all the effort where it would do most good.

Maybe these comments, committed to paper to help me organize my thoughts will have some influence on producing better guideline risk criteria.



ESTABLISHED 1802



ESTABLISHED 1802

E. I. DU PONT DE NEMOURS & COMPANY  
INCORPORATED

P. O. Box 6090  
NEWARK, DE 19714-6090

ENGINEERING DEPARTMENT  
LOUVIERS BUILDING

May 6, 1988



#### DU PONT RISK CRITERIA

At the risk of becoming a bore, I have attached yet another note on risk criteria.

I have not thought so much about criteria since I was responsible for developing the FAR target for [redacted] early in the 1970s. At that time I, like many others who have been involved in quantitative risk assessment for only a year or two, was very naive, not recognizing many of the problems.

We were fortunate that the FAR target worked because reducing individual's risks to the target never cost us money that we couldn't afford. Nevertheless, I was asked to write notes for VPs on more than one occasion to prove this.

However, when we tried to extend our criteria to transportation, major accidents and risks to the public, we were never able to find a suitable number or set of numbers which satisfied our needs. We tried using numbers, bands, grey areas, FN curves, ranges, but none could stand all the tests.

The fact of the matter is that every safety improvement is done to save lives, reduce injuries, prevent damage both to plant and environment, and prevent outrage. We make whatever improvements someone judges to be appropriate and no more.

2  
May 6, 1988  
[REDACTED]

That judgment may well be influenced by the person making the decision, the state of the business, and by some arbitrary criterion as well as the knowledge of the consequences but nevertheless that precise sum of money and no more, is spent at that time.

I would suggest that, no matter how difficult or emotional, we should recognize the fact that by so doing we are implicitly putting values on life, environment, outrage, etc. And there is nothing to be ashamed of in doing it explicitly, although there may be a need to convince people of this fact.

We shall then be making a better contribution to safety than by retaining or extending our current arbitrary parameters.

We would also eliminate much of the confusion over how to use and interpret our current targets.

I have directed these notes of the past few days to the people I consider most relevant and if I have your general support, I should be pleased to help initiate any appropriate action. [REDACTED] suggested that he and I might redraft S&OH Guideline 6.6 in an attempt to introduce some of these ideas whilst preserving the best of the past.

ENGINEERING SERVICE DIVISION  
Air Quality and Hazards Evaluation  
[REDACTED]  
[REDACTED]

3  
May 6, 1988  
[REDACTED]

EVEN MORE ABOUT PHI

Regardless of whether we consider the PHI of a small system or a total integrated plant site, improving the PHI:

from 100 to 10,000 saves 0.0099 lives per year  
from 1,000 to 10,000 saves 0.0009 lives per year  
from 5,000 to 10,000 saves 0.0001 lives per year

So, improving the PHI from x to y will always provide the same benefit (namely save the same number of lives) regardless of the system being analyzed and improved. At first sight that would indicate the same expenditure on improvement would always be justified. However, although lives lost is one measure of risk, it is accepted that public outrage is an added (and possibly dominant) loss and so preventing that outrage is an additional benefit that can be used to justify expenditure.

So, let us take say \$10MM for the minimum cost of a single life in a small accident.

Now consider say 100 lives in a large accident and assume we put the Du Pont Company (say \$30MMM) at risk with this. Now our cost per life at the other extreme of the scale is (\$30MMM + 100 x \$10MM) + 100 = \$330MM.

We now have a range of values for life depending upon the circumstances namely \$10-330MM.

Assuming we require a 10% return on investment and reverting to our PHI table, improving the PHI from -

100 to 10,000 saves 0.0099 lives/yr and justifies spending from \$1MM-33MM

1,000 to 10,000 saves 0.0009 lives/yr and justifies spending from \$90M-3MM

5,000 to 10,000 saves 0.0001 lives/yr and justifies spending from \$10M-330M

You will note that the PHI value tells you nothing about the size of the incident or the public outrage factor. So whereabouts in the spending range is a justified expenditure depends on the specific incident and not on the PHI.



4  
May 6, 1988  
[REDACTED]

Conclusion

The arbitrary PHI target serves little purpose in directing resources towards cost effective improvements in safety.

The only reliable way to achieve optimum safety is to make risk benefit analyses for each case.

After all, we are doing a risk benefit analysis implicitly with every safety improvement, whether we make it or reject it, whether we use numbers or not. Doing it explicitly simply means we get the best out of every situation and for the company as a whole.

NOTE: You may not agree with the numbers I have used, but these can be negotiated. The main purpose of the note is to demonstrate the principle.

## **Appendix F: Hard Pipe to Flexible Hose Transition Correspondence**

*(Documents in this appendix are redacted for confidentiality by black and white out)*

### **List of Acronyms, Abbreviations and Terminology**

AgProducts	The Agricultural Products Department/Business of DuPont
dry phosgene	liquid phosgene without any water, also called "anhydrous" phosgene
engg spec	engineering specification
ESD	Engineering Services Division of DuPont
SS	stainless steel

INTEROFFICE MEMORANDUM

Date: 9-Jul-1987 06:23pm  
From: [REDACTED]  
Dept: APRODUCTS  
Tel No: [REDACTED]

DuPont Belle Plant  
MAY 17 2010

TO: See Below

Subject: SLM'S PHOSGENE CYLINDER PIGTAILS

We have had several incidents where the brass fittings on the pigtails connecting the copper tubing to the phosgene cylinder valve has failed. The latest occurrence was on 7/5/87. In all cases only minor amounts of phosgene were released to the atmosphere and the failures typically, although not always, occurred while a fully protected operator had switched cylinders and was reconnecting the pigtails.

I sent a sample of a damaged brass fitting to Metallurgical lab to be evaluated by [REDACTED] and [REDACTED]. Their conclusion was that the brass was failing due to chemical attack by the ammonium hydroxide we use to detect leaks. The practice of spraying ammonium hydroxide on the brass along with the stress of tightening the fittings resulted in stress corrosion cracking (SCC). [REDACTED] recommends going to Monel 400 which is immune to SCC. He also recommends replacing the copper tubing with braided hose made of a corrugated Monel core with Monel external braiding. I believe that Laporte uses a monel-braid covered Teflon hose. The Laporte plant was considering testing a Kynar-braid covered Teflon hose because of discoloration and gradual deterioration of the Monel. One point to make about these hoses is that they are not easily fabricated and poor fabrication will lead to an increase in minor phosgene releases. I will work with [REDACTED] and the Laporte plant to come up with our best option.

Another point which was brought [REDACTED] and [REDACTED] brought up was the fact that the valve on the phosgene cylinders are also made of brass. I talked with [REDACTED] of PFG in Laporte about their leak detection methods. Apparently the spraying of ammonium hydroxide is the commonly accepted method for pinpointing phosgene leaks sources. At PFG they use a ~10-15% ammonium hydroxide solution to detect leaks. They recognize the problems with brass and ammonium hydroxide so their "pigtails" & connections are not made of brass. However, they have never experienced any problems with the brass valves on the cylinders possibly because of the size (thickness?) of the valves. The valves are also changed out on a ~1-2 year frequency. Dupont's Laporte plant uses braided hose as mentioned above and the ammonium hydroxide is not a problem.

Recommendations

Item	Responsibility
0 Replace all brass fittings on a monthly frequency. The "old" fittings will be sent to the Met. lab for visual & dye penetrant inspection for SCC. If evidence of SCC is	[REDACTED]

found, the frequency of replacement will be increased.

- 0 Replace existing ammonium hydroxide "squeeze bottles" with spray bottles. The squeeze bottles deliver a liquid stream while a spray bottle can deliver a vapor/mist. This will minimize the contact between the ammonium hydroxide and the brass. [REDACTED]
- 0 Verify that our procedures requires use of a dilute (10-15%) ammonium hydroxide solution. [REDACTED]
- 0 Incorporate the following steps in the leak detection procedure for the cylinder shed: [REDACTED]
  - 1. Carefully inspect brass fittings for damage before connecting cylinders. Any questionable fittings should be replace with new ones.
  - 2. After reconnecting pigtails, use Monitox to determine if phosgene is present. If the Monitox does not register any phosgene around fittings, then use of ammonium hydroxide is not required.
  - 3. If phosgene is detected, then use the ammonium hydroxide mist to pinpoint leak.
- 0 Train operators on the above procedure and emphasize the need to inspect brass fittings before reconnecting cylinders. [REDACTED]
- 0 Coordinate efforts with [REDACTED], [REDACTED] and Laporte plant personnel to develop optimum material of construction and design for phosgene pigtails and connections. [REDACTED]

Distribution:

- TO: [REDACTED] ( [REDACTED] )
- TO: [REDACTED] ( [REDACTED] )
- TO: [REDACTED] ( [REDACTED] )
- CC: [REDACTED] ( [REDACTED] )
- CC: [REDACTED] ( [REDACTED] )
- CC: [REDACTED] ( [REDACTED] )
- CC: [REDACTED] ( [REDACTED] )
- CC: [REDACTED] ( [REDACTED] )
- CC: [REDACTED] ( [REDACTED] )

DuPont Belle Plant  
MAY 17 2010

INTEROFFICE MEMORANDUM

Date: 14-Jul-1987 10:33am  
From: [REDACTED]  
Dept: ESD  
Tel No: [REDACTED]

TO: Remote Addressee ( [REDACTED] )  
CC: Remote Addressee ( [REDACTED] )  
CC: Remote Addressee ( [REDACTED] )  
CC: Remote Addressee ( [REDACTED] )

Subject: PHOSGENE SYSTEM

I appreciate receiving the copy of your program to improve the materials of construction and handling of phosgene at SLM. I'd like to make a few comments on the subject:

1. My point in the letter to [REDACTED] about the copper tubing used in the unloading system was that it would probably be OK as is but it seems we could do better (using hoses, etc.). However, we should concentrate on the integrity of the fittings, that being the immediate problem, and work out a program for the tubing later.

Monel is the preferred material of construction for fittings in both chlorine and phosgene cylinder unloading systems. Repeated use from numerous hook-ups may result in thread damage of the fittings, but corrosion and, more importantly, stress corrosion cracking (SCC) is not a concern. I strongly recommend that you move immediately to replacing the existing brass fittings with Monel and eliminate this hazard.

2. Reports from Laporte that Monel braided hoses were corroding in phosgene service are not exactly true, according to [REDACTED], ESD Materials Engineering, who covered the plant during the time Laporte was developing a program for these hoses. The hoses at that time were Teflon lined, with a Monel outer braid. Due to permeation of phosgene through the Teflon, the Monel was slightly attacked, forming a green surface film known as a "patina" which is common to all copper-based alloys.

3. Laporte supposedly changed to Teflon lined hose with an external braiding of Kynar, at least to address this discoloration "problem". I have not heard of their experience with this type of hose. They use Monel corrugated inner lining with an external Monel braid for chlorine service, mainly because it conforms to Chlorine Institute specifications. The supplier of both types of hoses is Triplex in Houston (contact is [REDACTED]), who has been "educated" as to the correct fabrication

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The following paragraphs describe SCC of copper alloys by ammonia which you can use in your formal contact with PPG regarding their use of brass valves on phosgene drums:

Stress corrosion cracking (SCC) is a corrosion phenomena that involves the synergistic effect of stress and corrosion to bring about the failure of components fabricated of a susceptible alloy. Chloride SCC of austenitic stainless steels is a common example of this in the chemical processing industry. Lesser known but equally hazardous is ammonia cracking of copper-based alloys. In earlier times this was commonly associated with brass in what was called "season cracking" of rifle cartridge cases; however, it is now known to affect any stressed copper-based alloy.

Metallographic examination has confirmed ammonia SCC of brass fittings that were removed from your phosgene unloading system. The ammonia exposure resulted from spraying the fitting joints with ammonium hydroxide for leak detection. The time-to-failure once the SCC conditions are met is extremely variable and depends on, among others, stress level and corrodent ion concentration.

Reducing the risk of SCC can certainly be helped by reducing the extremes - for instance, by reducing stress, by avoiding long time exposure by frequent replacement of affected parts, or by lowering the concentration of the corrodent. However, the solution to SCC problems is best accomplished by removing one of the variables of the SCC equation -

1. Stress - in this case, residual stress in (any) fittings or applied stress from use can hardly be avoided.
2. Corrodent - apparently, ammonium hydroxide is commonly used for leak detection in phosgene systems.
3. Material - Here we can avoid the problem by upgrading materials to Monel 400, a nominally 65% nickel, 30% copper alloy which is essentially immune to ammonia SCC and also offers good corrosion resistance to HCl (wet phosgene).

If I can help out in any way, please call.

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INTEROFFICE MEMORANDUM

Confidential

Date: 5-Aug-1987 04:30pm  
From: [REDACTED]  
Dept: AGPRODUCTS  
Tel No: [REDACTED]

DuPont Belle Plant  
Aug 7 2010

TO: Remote Addressee ( [REDACTED] )  
CC: [REDACTED] ( [REDACTED] )  
CC: [REDACTED] ( [REDACTED] )  
CC: [REDACTED] ( [REDACTED] )

Subject: Laporte's Phosgene Hose

I sent an informal survey to Laporte to determine what they use for phosgene "pig tails". The questions and responses are as follows:

1. Please provide a simple description of your phosgene handling and operation. This will allow a better understanding of your design and process needs versus ours.  
\* Simple diagram to be sent via FAX.
2. What is the frequency of cylinder changes?  
\* 3-4 times/day
3. What unloading nitrogen pressure do you use for phosgene?  
\* 165 psig
4. What is material of construction of hoses or piping that connects the cylinders to the process?  
\* Hose is Teflon lined with SS weld necks and SS overbraid.
5. What is length of hose, diameter and type of end fittings?  
\* To be sent via FAX.
6. What is frequency  
\* Hoses replaced every 3 months. Inspection and pressure testing of hoses done by manufacturer.
7. What materials and design with respect to hoses have you tried?  
\* Same hose design but with monel ends and overbraid.
8. What type of failures or leaks have you experienced with current

hoses and those which you may have used in the past.

\* Most failures due to fatigue from hose manipulation.

9. Have you considered using a corrugated monel core hose with monel external braiding, which is typical for chlorine service?

\* Yes, but concerns center around flexibility. Hoses must be able to bend 180 degrees and take the abuse of several changes a day.

10. How long has your current design (Hose) been in use. Are there any upgrades you would apply to this system?

\* 3-4 years in use. Contemplated Kynar overbraid but didn't use because of concern around fatigue failure. Would end up changing out hoses on some frequency and hoses are expensive.

11. Just out of curiosity, what type (model) and manufacturer of manual valves do you use in your phosgene system?

\* Engg Spec - T35E Globe Valve - which is the recommended chlorine service valve.

Based on the response from Laporte, it is still possible to use the monel corrugated hose you recommended since we would not apply undue bending stresses. However, we may be applying some twisting stresses as the nut is tightened onto the cylinder valve. Do you still consider this hose as a good candidate or are we better off using SS like Laporte and changing out the hoses on a 3 month interval?

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MAY 17 2010



DuPont -  
Cr

INTEROFFICE MEMORANDUM

DuPont Belle Plant  
MAY 17 2010

Date: 6-Aug-1987 07:40am  
From: [REDACTED]  
DeptNo: [REDACTED] URAL PROD DEPT

TO: [REDACTED] ( [REDACTED] )  
CC: [REDACTED] ( [REDACTED] )  
CC: [REDACTED] ( [REDACTED] )  
CC: [REDACTED] ( [REDACTED] )

Subject: RE: Laporte's Phosgene Hose

[REDACTED], you asked a lot of good questions in the questionnaire, but the one that appears to be missing is whether their hose failure frequency is better or worse than ours. I do not think that changing the type of hose we use on our cylinders is one that we can make over an electronic device such as this. I think we need to put down the key factors to consider for each type of hose that we feel is a candidate (which is what I believe that you are doing). Things like resistance to attack by phosgene and ammonium hydroxide, resistance to failure due to external stresses applied, expected failure frequency from whatever cause, frequency of change-out required, cost, availability of supply, etc. Then we ought to get the involved parties together to talk about making a change to be sure that we have not missed something. A change from what we are using may very well be in order, but again I caution that we need to be very certain that we are not making changing to something that is not as good as what we have now. We have to remember that what we are looking at is probably the "weakest link" in a system that routinely handles a very hazardous material. So far I think that the approach you are taking is fine. While we evaluate and make the decision, we need to be absolutely sure that we are replacing what we have frequently enough to assure that we will not have any kind of incident from its use.

INTEROFFICE MEMORANDUM

Conf-B  
Confid

Date: 12-Aug-1987 08:03pm  
From: [REDACTED]  
Dept: [REDACTED]  
Tel No: MAY 4 9 2010 [REDACTED]

TO: Remote Addressee ( [REDACTED] )  
CC: Remote Addressee ( [REDACTED] )  
CC: Remote Addressee ( [REDACTED] )  
CC: Remote Addressee ( [REDACTED] )

Subject: PHOSGENE HOSES

I finally got a chance to look at the message you sent about LaPorte's use of phosgene hoses - sorry this reply is so late.

I still believe that Monel is the best choice for material of construction for phosgene unloading hoses (and definitely for fittings). I am surprised that LaPorte is using Teflon-lined hose with stainless overbraid since Teflon is known to be permeable and the phosgene will attack the stainless. But the reason is that they replace them every 3 months because of fatigue problems. Fatigue to the point of hose failure is directly related to the applied stress and the quality of hose construction and is for the most part independent of the material of construction when the candidates are Monel or stainless steel.

Admittedly, the Monel hose will cost more than its stainless counterpart. However, with proper construction, and design so that stresses are minimized (no bends in the hose, a solid jumper used at the cylinder valve so that no torque is applied to the hose), useful life should be much greater than 3 months. Costs will be less in the long run and safety will also be improved.

INTEROFFICE MEMORANDUM

Date: 5-Feb-1989 01:16am  
From: [REDACTED]  
Dept:  
Tel No:

TO: [REDACTED]  
TO: [REDACTED]

DuPont Belle Plant  
MAY 17 2010

Subject: RE: Phosgene Handling

From: NAME: [REDACTED]  
FUNC: [REDACTED]  
TEL: ([REDACTED]) [REDACTED]

Materials compatibility with phosgene:

1. Quote from a publication by [REDACTED], retired Principal Materials Engineering Consultant:

"Phosgene - reacts violently with aluminum, particularly when wet. When wet, can stress crack and corrode austenitic stainless steels (304, 316, etc.). Has cracked stainless steel braid on Teflon transfer hoses. Also has corroded stainless steel cage in Teflon heat exchangers. Ferric chloride formed in phosgene lines has pitted through Incoloy 800 heat exchanger tubes. Natural rubber, neoprene, butyl, and buna N elastomers are unsatisfactory. Hypalon is resistant. Steel is satisfactory for dry phosgene."

2. NACE Corrosion Data Survey shows only the following for phosgene:

Good for steel and cast iron when anhydrous up to 200 F. Marginal resistance (<20 mpy) by 304/316, copper, and bronze up to 200 F when anhydrous. Unacceptable at less than 100% concentration.

Copper-nickel acceptable up to 200 F when anhydrous. Acceptable at 95% concentration at room temperature.

Monel and Nickel 200 acceptable up to 300 F when anhydrous.

Hastelloy B-2 and C-276 acceptable at 300 F at 10% concentration.

Aluminum has unacceptable corrosion rates at all temperatures and concentrations except anhydrous, where it is good to 200 F.

3. Metals Handbook, volume 13, "Corrosion":

"Under most conditions, particularly at room temperature, aluminum alloys resist halogenated organic compounds, but under some conditions, they may react rapidly or violently with some of these chemicals. If water is present, these chemicals may hydrolyze to yield mineral acids that destroy the protective oxide film of aluminum."

Based on this I would say that you should avoid using aluminum in the presence of phosgene. I do not know what special conditions

are needed to cause the rapid reaction or explosion of phosgene with [REDACTED], but I can certainly find out if you need more info. Corrosion may still be a problem, though, if it is diluted with water and may preclude its use anyway.

The Hastelloy and Monel diaphragms should be inspected occasionally, at least initially, to see how they are doing, but I wouldn't expect a corrosion problem with them unless they see phosgene at less than 100% concentration. Service in this case would be unknown - the data I have on these materials below 100% is incomplete.

Aluminum with alkalies:

Aluminum is not recommended for use or in the presence of any hydroxide solution. The corrosion rate is extremely rapid - ask American Airlines!

[REDACTED]

7/1/11

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MAY 17 2010

## **Appendix G: PHA Recommendation Delay Letter**

*(Documents in this appendix are redacted for confidentiality by black and white out)*

### **List of Acronyms, Abbreviations and Terminology**

COCL2	Phosgene
FEL	Front-end loading
PM	Preventive Maintenance
Rec	Recommendation
Rx	Reactor

To:  
(for approval)

Date 5/17/05

From:

PHA Recommendation Delay

Area Reviewed: SLM Front End

Year of PHA: 2004

Recommendation ID: 8, 15, 21

Original Due Date: 12/31/05

New Due Date: 12/31/06

Original Recommendation:

8. Complete 2003 Building PHA Recommendation #2.

15. Provide appropriate mitigation to prevent multiple fatalities from the release of a 2000 lb phosgene cylinder.
21. Provide appropriate mitigation to prevent multiple fatalities from phosgene release as a result of vaporizer tube failure.

Hazard:

8. Fatality from rupture of Rx2, or Rx5, or from phosgene release.
15. Multiple fatalities on and off site from large phosgene release.
21. Fatality from phosgene release

Deficiency:

8. If #2 vent header is being used to purge phosgene from Rx2 or Rx5 for emergency repair of a leaking flange, low eductor flow could cause backflow of water into the reactors and cause reaction of [REDACTED] and water in reactor and rupture. Also, if #2 vent header is being used to purge phosgene from phosgene system, backflow of water into the phosgene lines could cause corrosion and failure of the phosgene piping.
15. If the full phosgene cylinder were moved with hoist in error instead of the empty cylinder, the phosgene pipes would break and up to 2000 lbs of phosgene could be released.

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21. If there were a vaporizer tube leak during phosgene cleanout, steam pressure would be higher than vaporizer pressure, and steam ingress into the shell side of vaporizer could occur, causing corrosion and failure of the vaporizer. One layer of protection is material of construction of tubes makes tube leak highly unlikely, and there is a PM program for the tubes.

Interim Measures To Be Followed (If none, why not?)

The current operating procedures and practices help prevent any issues with the above deficiencies. After a cleanout of the vaporizer, the system is pressure tested, so if there was an issue with the tubes corroding this is one potential way to detect this issue. A COCl<sub>2</sub> generation system is currently being evaluated, and if this was installed the shed enclosure may be designed differently to handle the appropriate chemicals.

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To:  
(for approval)

Date 12/20/06

From:

PHA Recommendation Delay

Area Reviewed: SLM General Building

Year of PHA: 2004

Recommendation ID: 8,15,21

Original Due Date: 12/31/05

Extended Due Date: 12/31/06

New Due Date: 12/31/08

**Original Recommendation:**

8. Complete 2003 Building PHA Recommendation #2
15. Provide appropriate mitigation to prevent multiple fatalities from the release of a 2000 lb. phosgene cylinder.
21. Provide appropriate mitigation to prevent multiple fatalities from phosgene release as a result of vaporizer tube failure.

**Hazard:**

8. Fatality from rupture of Rx 2, or Rx 5, or from phosgene release
15. Multiple fatalities on and off site from large phosgene release
21. Fatality from phosgene release.

**Deficiency:**

8. If # 2 Vent header is being used to purge phosgene from Rx 2 or Rx 5 for emergency repair of a leaking flange, low eductor flow could cause backflow of water into the reactors and cause reaction of [redacted] and water in reactor and rupture. Also, if #2 vent header is being used to purge phosgene from phosgene system, backflow of water into the phosgene lines could cause corrosion and failure of the phosgene piping.
15. If the full phosgene cylinder were moved with hoist in error instead of the empty cylinder, the phosgene pipes would break and up to 2000 lbs. of phosgene would be released.
21. If there were a vaporizer tube leak during phosgene cleanout, steam pressure would be higher than vaporizer pressure, and steam ingress into the shell side of vaporizer could occur, causing corrosion and failure of the vaporizer. One layer of protection is material of construction of the tubes, making tube leak highly unlikely, and there is a PM program for the tubes.

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**Why Can Extended Due Date Not Be Met?**

Work to define the scope on this item is progressing but not yet complete. We are evaluating potential lower cost alternatives to total shed enclosure.

**Summary of Progress To Date:**

- Initial front-end loading was completed and a [REDACTED] prepared to install an enclosed phosgene shed with scrubber.
- Facilities have been changed and procedures put in place to disconnect Rx 2 & Rx 5 from # 2 vent header except for emergency situations and install a Class B interlock to prevent liquid backflow into #2 Vent header. This closes the first deficiency of 2004 PHA Rec. 8.

**Interim Measures To Be Followed (If none, why not?)**

The current operating procedures and practices help prevent any issues with the above deficiencies. After a cleanout of the vaporizer, the system is pressure tested, so if there were an issue with the tubes corroding, this is one potential way to detect this issue.

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To: [REDACTED]  
(for approval)

Date: 12/3/08

From: [REDACTED]

PHA Recommendation Delay

Area Reviewed: SLM Front End

Year of PHA: 2004

Recommendation ID: #15

Original Due Date: 12/2005

New Due Date: 11/30/09

- Original Recommendation: Provide appropriate mitigation to prevent multiple fatalities from the release of a 2000 lb phosgene cylinder.

Why Can Original Due Date Not Be Met? The project is in FEL3 and the schedule indicates completion by August 2009.

Summary of Progress To Date:

The capital project completed most of FEL2 in 2003 but was placed on hold. A Blackbelt study was done in 2005. The capital project was reactivated in 2006 and again placed on hold. The capital project was reactivated again in 2008. The holds on the capital project were due to uncertainty of the future of the facility and due to the cost of the project.

Interim Measures To Be Followed (If none, why not?)

None. No interim measures were identified by the Blackbelt project.

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RGA 8/30/00

Date : 11/18/09

To : [REDACTED] \_\_\_\_\_  
[REDACTED] \_\_\_\_\_  
[REDACTED] \_\_\_\_\_  
From : [REDACTED] \_\_\_\_\_

PHA Recommendation Extension Request

Area Reviewed : SLM General Building  
Year of PHA : 2004  
Recommendation ID : 15, 21  
Original Due Date : 12/31/05  
Extended Due Dates : 12/31/06, 12/31/08, 11/30/09  
New Due Date : 11/30/2010

Original Recommendations :

15. Provide appropriate mitigation to prevent multiple fatalities from the release of a 2000lb. phosgene cylinder.
21. Provide appropriate mitigation to prevent multiple fatalities from phosgene release as a result of vaporizer tube failure.

Hazards :

15. Multiple fatalities on and off site from large phosgene release.
21. Fatality from phosgene release.

Deficiency :

15. If a full phosgene cylinder was moved with hoist in error instead of the empty cylinder, the phosgene pipes would break and up to 2000 lbs of phosgene would be released.
21. If there were a vaporizer tube leak during phosgene cleanout, steam pressure would be higher than vaporizer pressure, and steam ingress into the shell side of the vaporizer could occur, causing corrosion and failure of the vaporizer. One layer of protection is material of construction of the tubes, making tube leak highly unlikely, and there is a PM program for the tubes.

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**Why Can Extended Due Date Not Be Met ?**

During FEL 3 for a project to install a phosgene scrubber to address these recommendations, an error in basic data was discovered. This invalidated the original design basis for the scrubbing system, and required a halt to the project activity.

Since that time, a corporate team has been formed and chartered to determine the best means to address the recommendations. The completion date for the team to submit their plan is 11/30/09. The team charter is attached below.



**Summary of Progress To Date :**

The capital project completed most of FEL2 in 2003 but was placed on hold. A Blackbelt study was done in 2005. The capital project was reactivated in 2006 and again placed on hold. The capital project was reactivated again in 2008. The holds on the capital project were due to uncertainty of the future of the facility and due to the cost of the project.

Front End Loading (FEL) 1 & 2 was completed and a [REDACTED] prepared to install and enclosed phosgene shed with scrubber. The Basic Data error was discovered during FEL-3.

**Interim Measures To Be Followed (If none, why not?)**

1. Vaporizer is inspected annually - Last inspection was completed 10/09.
2. Hose assembly system is replaced every 6 months.
3. Hoses are pressure tested before installation.
4. Entire system is pressure tested before campaign start.
5. Procedures require pressure testing connection when cylinders are changed.

**PSM Program Compliance**

- Preventative Checks
- Special Procedures

**HTM Permit Process**

- Operator Training
- Up to Date Operating Procedures
- Phosgene Alarm at Cylinder Connection
- Cylinder Capping Kit/First Responder Training

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