U.S. Chemical Safety and
Hazard Investigation Board

DuPont La Porte, Texas Chemical Facility Toxic Chemical Release

Interim Recommendations

Investigation:	2015-01-I-TX
Incident Date:	November 15, 2014
Issue Date:	September 30, 2015

Staff draft that is subject to change, approval, or disapproval by the Board.

Whereas:

1. On November 15, 2014, nearly 24,000 pounds of methyl mercaptan[1] was released inside the Lannate®[2] unit at the E. I. du Pont de Nemours chemical manufacturing facility in La Porte, Texas ("DuPont").[3] The release resulted in the fatalities of three operators and a shift supervisor inside the Lannate® manufacturing building ("manufacturing building").[4] The four DuPont employees[5] died from a combination of asphyxia and acute exposure to toxic chemicals including methyl mercaptan.[6,7] All four victims were located inside the manufacturing building—three on the third floor and one descending the stairs between the third and second floor.[8]

2. Following Bhopal,[9] DuPont made significant modifications to its La Porte methyl isocyanate (MIC) process[10] that incorporated inherently safer design (ISD).[11] These ISD approaches included the use of an open building structure with equipment to direct leaks of highly toxic chemicals to an incinerator for destruction. However, DuPont did not effectively apply similar ISD to other chemicals it also classified as highly toxic, such as methyl mercaptan and chlorine. As a result, the methyl mercaptan release on November 15, 2014, inside an enclosed and unventilated building[12] contributed to the deaths of four DuPont employees.

3. The portion of the process where the incident took place is enclosed within a building that has no documented design function and appears to serve no essential manufacturing purpose. However,

---

[1] Methyl mercaptan is a highly toxic, highly flammable chemical that can cause asphyxiation in poorly ventilated areas. At room temperature (above 43 °F), methyl mercaptan is a colorless gas with an unpleasant odor described as rotten cabbage. *See* http://www.atsdr.cdc.gov/MHMI/mmg139.pdf (accessed June 15, 2015).

[2] Lannate® is the DuPont trade name for methomyl. Methomyl is an insecticide and is the generic name for S-methyl-N [(methycarbamoyl) oxy1] thioacetimaidate.

[3] The majority of the methyl mercaptan was initially released onto the third floor of the manufacturing building. In addition, some methyl mercaptan was likely released from nitrogen relief valves at each of the methyl mercaptan railcar spots.

[4] Three other workers were injured from their exposure to methyl mercaptan, and at least three additional workers experienced methyl mercaptan exposure symptoms.

[5] The victims included operators Robert Tisnado (39), Gilbert Tisnado (48), Crystle Wise (53), and shift supervisor Wade Baker (60).

[6] Methyl mercaptan is a chemical asphyxiant. Chemical asphyxiates are toxic agents that prevent red blood cells from carrying oxygen. Speegle, M. *Safety, Health, and Environmental Concepts for the Process Industry,* Second Edition.; Delmar: New York, 2013; p58.

[7] Symptoms of methyl mercaptan toxicity also include narcosis (a state of stupor, drowsiness, or unconsciousness), and cyanosis (blue or purple coloration of the skin or mucous membranes caused by inadequate oxygenation of the blood). Centers for Disease Control and Prevention, NIOSH Pocket Guide to Chemical Hazards - Methyl Mercaptan.
See http://www.cdc.gov/niosh/npg/npgd0425.html (accessed September 13, 2015).

[8] One victim on the third floor was located near a methyl mercaptan leak source on the wet end (east) side. The other two victims on the third floor were on the dry end (west) side.

[9] On December 3, 1984, a methyl isocyanate (MIC) release at the Union Carbide insecticide plant in Bhopal, India resulted in an estimated 3,800 people that died within days, and tens of thousands that were injured. Eventually, the release killed tens of thousands of people. See http://www.csb.gov/on-30th-anniversary-of-fatal-chemical-release-that-killed-thousands-in-bhopal-india-csb-safety-message-warns-it-could-happen-again-/?pg=4 (accessed June 17, 2015).

[10] MIC is a raw material used in the production of insecticides at La Porte including the Lannate® process.

[11] According to the Center for Chemical Process Safety (CCPS), "inherently safer design solutions eliminate or mitigate the hazard by using materials and process conditions that are less hazardous." Center for Chemical Process Safety (CCPS). Inherently Safer Chemical Processes – A Life Cycle Approach. 2nd ed., Section 5.1.1, 2009.

[12] At the time of the incident, the manufacturing building ventilation fans were not operating. This information is further detailed below.

Staff draft that is subject to change, approval, or disapproval by the Board.

housing the process equipment inside the enclosed manufacturing building exposed personnel to highly toxic chemical exposure and asphyxiation hazards that DuPont has not effectively identified or controlled.

4. The DuPont manufacturing building design introduces all of the increased personnel hazards, but offers none of the beneficial off-site risk reduction of a containment building.[13] The DuPont manufacturing building is not designed to limit the impact of a toxic chemical leak by containing the leak and routing it to a destruction device such as an incinerator or scrubber. Vapors from highly toxic chemical leaks are trapped and concentrated inside the building, increasing risk to workers. Additionally, by DuPont's design, the manufacturing building ventilation system discharges these highly toxic chemical leaks from the roof of the manufacturing building to the outdoor surroundings, resulting in no risk-reduction benefit to the public.

5. The manufacturing building ventilation fans were classified as critical process safety equipment by DuPont, meaning their failure could result in a high consequence event. A design objective of the ventilation fans was to "control contaminants to acceptable work place exposure levels." However, neither fan was in operation at the time of the incident. The CSB's preliminary calculations indicate that even with both fans operating, ventilation would likely have been insufficient to avoid a lethal atmosphere inside the manufacturing building because of the amount of toxic gas released.[14,15]

6. At the time of the incident, the manufacturing building ventilation fan for the portion of the unit where the methyl mercaptan was released (wet end fan) was not operating despite an "urgent"[16] maintenance work order written on October 20, 2014, nearly a month prior to the incident. The loss of the ventilation fan did not result in any additional safety precautions, such as enhanced operational or emergency response planning, restricted worker access to the manufacturing building, or increased personal protective equipment (PPE) requirements.

7. As a result of the release, the manufacturing building stairways were contaminated with highly toxic and highly flammable methyl mercaptan. The stairways were not a safe location for workers. However, these stairways provide the primary means to access the equipment or exit the building in the event of an emergency. The stairways are designed for fire escape, but DuPont has not effectively

---

[13] A containment building is an enclosure around process equipment to contain potential releases to the environment. Companies typically use containment buildings to reduce off-site risk. DuPont has stated that the Lannate® manufacturing building is not a containment building.

[14] The IDLH for methyl mercaptan is 150 parts per million (ppm). See http://www.cdc.gov/niosh/idlh/74931.html (accessed July 8, 2015). According to OSHA, "Immediately dangerous to life or health (IDLH) means an atmosphere that poses an immediate threat to life, would cause irreversible adverse health effects, or would impair an individual's ability to escape from a dangerous atmosphere." See https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=12716 (accessed July 8, 2015).

[15] For methyl mercaptan, the 10-minute AEGL-2 (disabling) is 40 ppm and the 10-minute AEGL-3 (lethal) is 120 ppm. "AEGL-2 is the airborne concentration (expressed as ppm or mg/m3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape. AEGL-3 is the airborne concentration (expressed as ppm or mg/m3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death." See http://www.ncbi.nlm.nih.gov/books/NBK201324/ (accessed September 22, 2015).

[16] While the timing to complete an "urgent" worker order is not specifically defined, based on CSB's review of DuPont records and interviews conducted with DuPont employees, it has a practical meaning of two to three days.

Staff draft that is subject to change, approval, or disapproval by the Board.

evaluated entry or exit for toxic gas hazards or in an oxygen-deficient environment.[17] There is no ventilation provided in the manufacturing building's stairways. Furthermore, the internal doors between those stairways and the process areas do not provide an effective barrier to keep hazardous gases released in the process areas from entering the stairways.

8. DuPont's methyl mercaptan detection system does not effectively warn workers or protect the public from highly toxic chemical exposure. The methyl mercaptan detector concentration alarm point is above the permissible exposure limit for workers[18] and DuPont's response to a detector alarm is not sufficient to protect the public. For example, during the hours prior to the November 15, 2014 incident, multiple highly toxic chemical gas detectors alarmed (sounded).[19] However, the DuPont emergency response team (ERT) was not notified and the area was not cleared of personnel. In addition, methyl mercaptan releases on November 13 and 14, 2014, were identified by methyl mercaptan detectors, but were never reported as releases nor investigated as serious process safety incidents.

9. DuPont's process hazard analyses (PHAs) and relief system design scenarios do not effectively identify hazards from nonroutine operations, such as opening valves to connect the liquid methyl mercaptan piping to the vapor waste gas vent header—the piping connection that provided the pathway for the methyl mercaptan release in this incident.[20] Along the methyl mercaptan feed line there were three locations where it was connected by valves to the waste gas vent header piping. At the time of the incident, one of these valves was fully open and a second valve was slightly open.

10. PHAs performed on the insecticide manufacturing process did not sufficiently identify and control process hazards. Post-incident, DuPont has conducted new baseline PHAs for two of its 15 Insecticide Business Unit (IBU) PHAs. These post-incident PHA teams applied a more robust hazard analysis methodology and, as a result, identified many new potential hazardous events and developed hundreds of associated corrective action items. DuPont has agreed to develop and implement a revised schedule to expedite the cyclical reviews for the remaining IBU PHAs, and the final schedule will prioritize high-hazard processes. Some of these PHAs will be redone prior to restart. In addition, DuPont has retained a third-party consultant to review the existing IBU PHAs prior to restart.

---

[17] Some portions of the manufacturing building can also be accessed by an elevator or with ladders.

[18] The methyl mercaptan detectors alarm at 25 parts per million (ppm) – well above the OSHA recommended permissible exposure limit (PEL) of 0.5 ppm and the OSHA enforceable PEL ceiling limit of 10 ppm. OSHA recommends that employers consider using the alternative occupational exposure limits because the agency believes that exposures above some of these alternative occupational exposure limits may be hazardous to workers, even when the exposure levels are in compliance with the relevant PELs. See https://www.osha.gov/dsg/annotated-pels/ (accessed June 15, 2015). The Cal-OSHA permissible exposure limit (PEL) is an 8-hour time weighted average (TWA) of 0.5 ppm and the NIOSH recommended exposure limit (REL) is a 15-minute ceiling limit of 0.5 ppm. See https://www.osha.gov/dsg/annotated-pels/tablez-1.html (accessed June 15, 2015).

[19] The methyl mercaptan gas detectors alarm on the Lannate® control room operator's computer screen. There is no audible or visible alarm provided in the field for outside personnel.

[20] The vapor waste gas vent header is piping intended to remove excess or unwanted vapor from the process and route it to an incinerator for thermal destruction (combustion).

Staff draft that is subject to change, approval, or disapproval by the Board.

11. The manufacturing building air dilution ventilation system has never been evaluated by a PHA or robust engineering analysis.

12. The area of the manufacturing building where the largest methyl mercaptan release occurred during the incident has never been tested for ventilation flow rate or effective distribution of dilution air. Although DuPont mechanical integrity procedures call for annual air flow testing, the manufacturing building ventilation system for the immediate area impacted by the methyl mercaptan release (the wet end fan) had never been tested for flow rate or effective distribution of dilution air.

13. The (IBU) process analyzer houses[21] are infrequently entered, but they are equipped with more robust asphyxiation safeguards (oxygen detectors and alarms) than the normally occupied manufacturing building. However, the manufacturing building—which lacks the same level of asphyxiation safeguards—has significantly larger inventories of hazardous chemicals, has unventilated areas, and is regularly occupied by workers.

14. DuPont has been in the process of implementing a five-year program at La Porte to validate that pressure relief systems comply with existing DuPont standards, process safety regulations, and industry codes and standards. DuPont has not made this program a sufficiently high priority and additional outside resources are needed for effective completion. Although the program is more than four years into the five-year plan, IBU relief systems are only 35% complete.

15. The CSB identified pressure relief systems in the insecticide manufacturing process that are improperly designed and do not meet the requirements of industry codes and standards. As a result, these relief systems do not effectively ensure that highly toxic, highly flammable, and asphyxiating chemicals are discharged to safe locations. For example, during the incident an atmospheric release of highly toxic and highly flammable liquid methyl mercaptan likely occurred through a relief system intended to release and disburse nitrogen vapor. This relief system is part of the 35% of systems DuPont considers complete and in compliance with industry codes and standards. However, the alignment of block valves at the time of the incident revealed a highly toxic methyl mercaptan release scenario that DuPont's five-year relief system compliance program never considered.

16. On June 11, 2015, the CSB investigation team concluded that DuPont planned to resume insecticide manufacturing operations at the facility in August 2015 without addressing the important process safety issues described above. The CSB investigation team informed DuPont officials that it would pursue recommendations to address the significant process safety issues identified. The CSB investigation has identified many significant process safety management issues at the La Porte facility. Throughout the investigation, as these process safety issues were identified, the CSB communicated and discussed these concerns with DuPont officials in order to promote needed improvements and prevent future similar occurrences. [22]

---

[21] Analyzer houses are small enclosed buildings to protect process analyzer equipment for improved reliability.

[22] The CSB raised many other process safety concerns to DuPont officials. Many of these process safety issues have been included in DuPont's pre-startup corrective actions. These additional process safety issues that DuPont agreed to address are outside the scope of this interim recommendations document, but will be further detailed in future CSB investigation work products.

Staff draft that is subject to change, approval, or disapproval by the Board.

17. On July 2, 2015, DuPont committed to addressing the process safety issues identified by the CSB. In a written statement provided to the CSB and certain media outlets on September 3, 2015, DuPont described the completion of their investigation into the November 15, 2014 incident. In this communication, DuPont also reiterated its commitment to implementing the CSB recommendations presented during the July 22, 2015 CSB public business meeting. DuPont also stated that the La Porte crop protection units will not restart until these actions have been completed. The CSB is encouraged by DuPont's commitment to address these recommendations. However, formal recommendations are being issued so that the Board can evaluate and track to completion DuPont's mitigation of the identified hazards.

18. Board procedures authorize the development and issuance of interim safety recommendations before a final investigation report is completed.

19. Process safety concepts including the important role of transparency between industry and the public in improving health and safety for the facility and the surrounding communities, active workforce participation, the hierarchy of controls, inherently safer design, reducing the risk of major accidents to the greatest extent feasible, effective safeguards, and nonroutine work are discussed, but not fully explained in this document. CSB analysis related to these process safety topics are more fully described in the CSB's DuPont Belle, Chevron Richmond, and Tesoro Anacortes investigation reports. Rather than repeat this information which is applicable to DuPont La Porte, these reports are incorporated into this CSB work product by reference. These reports can be accessed at www.csb.gov.

Staff draft that is subject to change, approval, or disapproval by the Board.

Accordingly:

Pursuant to its authority under 42 U.S.C. §7412(r)(6)(C)(i) and (ii), and in the interest of promoting safer operations at US facilities handling chemicals and protecting workers and communities from hazards, the Board makes the following interim safety recommendations to the DuPont chemical manufacturing facility in La Porte, Texas and the International Chemical Workers Union Council of the United Food and Commercial Workers:

DuPont La Porte, Texas Chemical Facility

2015-01-I-TX-R1

Inherently Safer Design Review

Prior to resuming Insecticide Business Unit (IBU) manufacturing operations, conduct a comprehensive engineering analysis of the manufacturing building and the discharge of pressure relief systems with toxic chemical scenarios to assess potential inherently safer design options. At a minimum, evaluate the use of an open building structure, and the direction of toxic chemical leaks and the discharge of pressure relief systems with toxic chemical scenarios to a destruction system. Implement inherently safer design principles to the greatest extent feasible and effectively apply the hierarchy of controls such that neither workers nor the public are harmed from potential highly toxic chemical releases. Detail the analysis, findings, and corrective actions in a written report and make this report available to DuPont La Porte employees, their representatives, and the CSB.

2015-01-I-TX-R2[23]

Ensure Manufacturing Building is Safe for Workers

Prior to resuming Insecticide Business Unit (IBU) manufacturing operations, conduct a robust engineering evaluation of the manufacturing building and the dilution air ventilation system that includes the implementation of corrective action(s) to the greatest extent feasible in order to ensure a safe environment for all workers. Develop a documented design basis for the manufacturing building and the air dilution ventilation system that identifies effective controls for highly toxic, asphyxiation, and flammability hazards and implement these controls to the greatest extent feasible. Address nonroutine operations and emergency response activities in the design basis. The design basis for the manufacturing building and the dilution air ventilation system must use the hierarchy of controls and inherently safer design principles to the greatest extent feasible.

[23] It is understood that depending on the mitigation approach taken by DuPont some aspects of recommendation R1 or recommendation R2 may not be applicable in the future. The CSB recommendations program provides sufficient flexibility to allow a recommendation to be "no longer applicable" following the CSB's recommendation evaluation process. For example, if DuPont moves the equipment containing highly toxic chemicals to an open outdoor structure to address recommendation R1 the evaluation of the air dilution ventilation system in recommendation R2 may no longer be applicable.

Staff draft that is subject to change, approval, or disapproval by the Board.

2015-01-I-TX-R3

Ensure Relief System Design is Safe for Workers and the Public

Prior to resuming manufacturing operations, ensure all Insecticides Business Unit (IBU) pressure relief systems are routed to a safe location and effectively apply the hierarchy of controls to protect workers and the public. Commission a pressure relief device analysis, consistent with API Standard 521 and the ASME Code, including a field review. Include an evaluation of relief system discharge location to ensure that relief systems are discharged to a safe location that will prevent toxic exposure, flammability, or asphyxiation hazards in order to ensure public and worker health and safety to the greatest extent feasible. Include an evaluation of relief scenarios consistent with API Standard 521.

2015-01-I-TX-R4

Perform More Robust Process Hazard Analyses

Develop and implement an expedited schedule to perform more robust process hazard analyses (PHAs) consistent with R1, R2, and R3 for all units within the Insecticides Business Unit (IBU). At a minimum, the PHAs must effectively identify and control the hazards referenced in this document utilizing the hierarchy of controls. The PHA schedule must be prioritized based on anticipated risks to the public and workers in order to ensure that the highest risk areas receive priority consideration. At a minimum, the more robust PHAs must be consistent with the approach applied to post-incident reviews described above in paragraph 10.

2015-01-I-TX-R5

Ensure Active Workforce Participation

Work together with the International Chemical Workers Union Council of the United Food and Commercial Workers (ICWUC/UFCW) Local 900C and the ICWUC/UFCW staff (at the request of the local) to develop and implement a plan to ensure active participation of the workforce and their representatives in the implementation of Recommendations R1 through R4. In addition, provide a copy of DuPont's integrated plan for restart to La Porte workers and their local union representatives.

2015-01-I-TX-R6

Public Transparency and Accountability

Make publicly available (on a website) a summary of the DuPont November 15, 2014 incident investigation report, the integrated plan for restart, and actions to be taken for the implementation of Recommendations R1 through R5. This website must be periodically updated to accurately reflect the integrated plan for restart and implementation of Recommendations R1 through R5.

Staff draft that is subject to change, approval, or disapproval by the Board.

International Chemical Workers Union Council (ICWUC) of the United Food and Commercial Workers (UFCW) and Local 900C

2015-01-I-TX-R7

Ensure Active Workforce Participation

Work together with DuPont to develop and implement a plan to ensure active participation of the workforce and their representatives in the implementation of Recommendations R1 through R4.

Staff draft that is subject to change, approval, or disapproval by the Board.

Appendix: Information to Support Recommendations

Incident Consequences

1. On November 15, 2014, nearly 24,000 pounds of methyl mercaptan[24] was released within the Lannate® unit at the DuPont La Porte chemical manufacturing facility ("DuPont") in La Porte, Texas.[25] Methyl mercaptan is a highly toxic, highly flammable chemical that can cause asphyxiation.[26]

2. The release resulted in the deaths of three operators and a shift supervisor inside the Lannate® manufacturing building ("manufacturing building"). The four DuPont employees[27] died from a combination of asphyxia and acute exposure to toxic chemicals including methyl mercaptan. All four victims were located inside the manufacturing building—three on the third floor and one descending the stairs between the third and second floor.[28]

3. Due to the extremely low odor threshold[29] of methyl mercaptan,[30] portions of the greater Houston area downwind of the facility detected the release, but no off-site injuries have been reported.

Process Overview

4. DuPont has several business units located at the La Porte, Texas, facility. Each unit is focused on a different chemical business area. The incident took place in the Insecticide Business Unit

[24] At room temperature (above 43 °F), methyl mercaptan is a colorless gas with an unpleasant odor described as rotten cabbage. Exposure in poorly ventilated, enclosed, or low lying areas can result in asphyxiation. See http://www.atsdr.cdc.gov/MHMI/mmg139.pdf (accessed June 15, 2015).
[25] The majority of the methyl mercaptan was initially released onto the third floor of the manufacturing building. In addition, methyl mercaptan was likely released from each of the nitrogen relief valves at the methyl mercaptan railcar spots.
[26] DuPont's corporate standard for the management of highly toxic materials identifies both methyl mercaptan and chlorine as highly toxic. DuPont considers a material to be highly toxic if it is handled, stored, or shipped in a sufficient quantity that, as the result of a credible event could result in an ERPG-3 concentration, and has a substance hazards index (SHI) greater than or equal to 4,000. DuPont determines the SHI using vapor pressure and ERPG-3 data for each chemical. Using this approach, DuPont derived a SHI of 19,855 for methyl mercaptan and 385,197 for chlorine.
[27] The victims included Crystle Wise (53), Robert Tisnado (39), Gilbert Tisnado (48), and Wade Baker (60).
[28] One victim on the third floor was located near a methyl mercaptan leak source on the wet end (east) side. The other two victims on the third floor were on the dry end (west) side.
[29] Odor threshold, in general is the lowest concentration of a gas or a material's vapor that can be detected by odor. Odor threshold values are not fixed physiological parameters or physical constants but are statistical points representing the best estimate value from a group of individual responses. Murnane, Sharon, S.; Lehocky, Alex, H.; Owens, Patrick, D. *Odor Thresholds for Chemicals with Established Occupational Health Standards*, Second Edition; AIHA: Falls Church, Virginia, 2013; p 2.
[30] The odor threshold for methyl mercaptan is approximately two parts per billion (2 ppb). However, olfactory fatigue is known to occur with methyl mercaptan, resulting in the exposed person to no longer being able to detect the chemical by smell. As a result, odor may not provide adequate warning of hazardous concentrations. See http://www.atsdr.cdc.gov/MHMI/mmg139.pdf (accessed June 15, 2015).

Staff draft that is subject to change, approval, or disapproval by the Board.

(IBU).[31] Portions of the IBU process units are located inside a four-story, enclosed manufacturing building shown in Figure 1.

Figure 1. East side of the manufacturing building at the DuPont La Porte insecticide production facility.

5. The IBU is divided into two primary insecticide product lines, displayed on the unit insignia located on the outside wall of the manufacturing building (Figure 2):[32] Lannate®, which is DuPont's trade name for methomyl[33]; and Agricultural Products Intermediates (API), which produces insecticides and nematicides known as Vydate®, the trade name for oxamyl.[34]

6. Both the Lannate® and Vydate® product lines use methyl mercaptan as an intermediate raw material in the production of insecticides. The incident took place within the Lannate® area of the process.[35,36]

[31] In addition to the IBU, the facility has a Herbicides Business Unit (HBU) and a Fluoroproducts Business Unit (FBU). The FBU includes a anhydrous hydrogen fluoride (HF) manufacturing unit. FBU assets were transferred to Chemours on July 1, 2015.
[32] The IBU processes share a common control room.
[33] Methomyl is the generic name for S-methyl-N [(methycarbamoyl) oxy1] thioacetimaidate.
[34] Oxamyl is the generic name for Methyl 2-(Dimethylamino)-N-Hydroxy- 2-Oxoethanimidothioa. In addition to being an insecticide, oxamyl also functions as a nematicide. "Plant parasitic nematodes are among the most important crop pathogens in the United States, causing an estimated $7-9 billion in lost yield annually." See https://www.sbir.gov/sbirsearch/detail/147642 (accessed July 17, 2015).
[35] Lannate® and API are not in distinctly different locations. At some points, Lannate® and API equipment are side by side.
[36] The IBU is further subdivided into four functional areas: the wet end, MIC (methyl isocyanate), the damp end, and the dry end. The wet end contains liquid reaction equipment. MIC contains equipment to generate and consume the methyl isocyanate

Staff draft that is subject to change, approval, or disapproval by the Board.

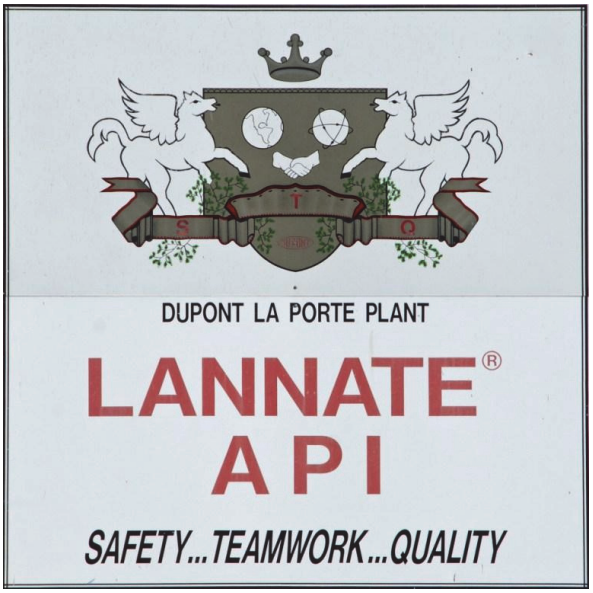

Figure 2. Sign on the outside wall of the manufacturing building showing the two primary product lines – Lannate® and API (Vydate®) for the IBU at the DuPont La Porte facility.

Manufacturing Building Ventilation Design

7. The main portion of the manufacturing building is separated on each floor by an internal wall. The east side of the wall is where liquids processing equipment is located and is referred to as the "wet end." The west side of the wall is where liquids are removed via damp and dry processing equipment and is referred to as the "dry end." The Vydate® product is a liquid, while the Lannate® products are powders.

8. Inside the manufacturing building, the internal wall that separates the east and west sides is equipped with fire doors that allow worker access between the wet and dry ends, as shown in Figure 3. By design, these doors are intended to be closed, but at times the doors were left propped open. In addition to adversely affecting the fire protection design, opening the doors provides a path for released chemicals on one side of the room to infiltrate to the other side.

intermediate. The damp end isolates and dries insecticide crystals. The dry end processes the crystals and packages them into various products.

Staff draft that is subject to change, approval, or disapproval by the Board.

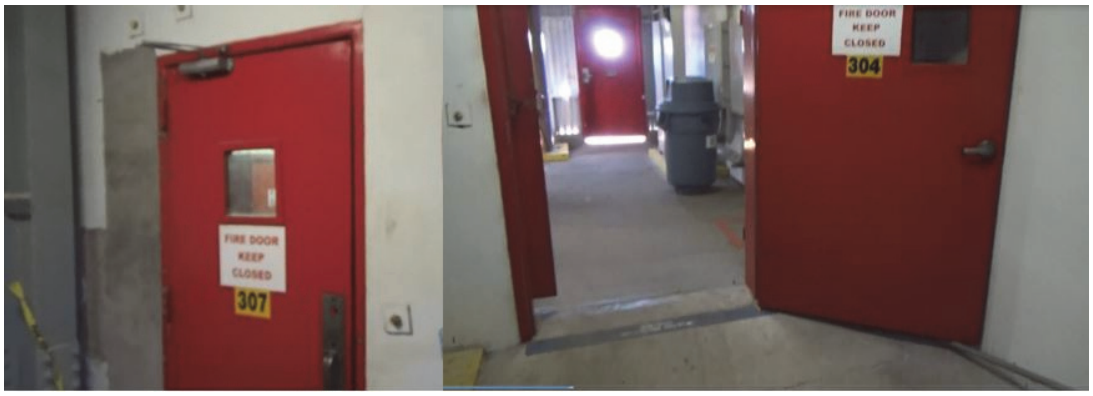

Figure 3. Doors within the manufacturing building on the 3rd floor that separate the east (wet end) and west (dry end) sides. Although intended by design to remain closed, these doors were propped open at times, as shown in the photograph of door 304 on the right.

Figure 4. Roof of the manufacturing building showing the dry end fan (left), wet end fan (right), and location of the internal wall (middle) that separates each side within the building.

9. The two sides of the building are separately ventilated by fans located on the roof of the building as shown above in Figure 4. The manufacturing building is designed to make use of these roof-mounted fans via a dilution air ventilation system that operates as shown in Figure 5 through Figure 8. Fresh air is drawn into each floor on each side of the building, entering at floor level through a mechanical louver system.[37] Air is designed to flow from the fresh air louvers, across

[37] The louver is a set of angled slats or flat strips fixed or hung at regular intervals in a shutter to allow air to pass through.

Staff draft that is subject to change, approval, or disapproval by the Board.

the process equipment, and up into return ducts located at the ceiling along the internal wall to sweep away any flammable gases.[38] Exhaust air on each side of each floor moves inside the ceiling-mounted duct towards the north end of the building (Figure 5 and Figure 7), where it is collected in a vertical duct header that directs the exhaust air from all of the floors on each side up towards the respective (wet or dry end) dilution air exhaust fan on the roof (Figure 6 and Figure 8). Exhaust air from the fans is discharged directly to atmosphere. Contaminants are not removed via any kind of environmental destruction system such as a scrubber or incinerator.

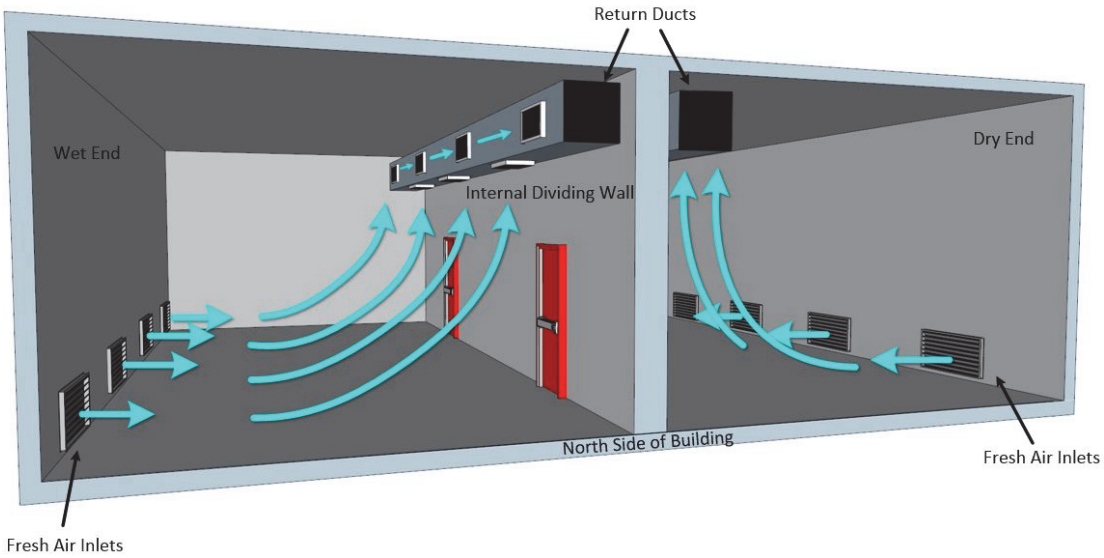

Figure 5. Simplified graphic representation of a typical floor of the manufacturing building showing how fresh air is pulled in from the outside walls, sweeps across the floor, and enters the exhaust return air ducts on each side.

[38] DuPont records indicate that the manufacturing building ventilation system design code is NFPA 497, Recommended Practice for the Classification of Flammable Liquids, Gases, or Vapors and of Hazardous (classified) Locations for Electrical Installations in Chemical Process Areas. NFPA 497 defines adequate ventilation as being sufficient to ensure that the concentration of flammable gases does not exceed 25 percent of the lower explosion limit (LEL). DuPont's methyl mercaptan safety data sheet (SDS) indicates that the LEL for methyl mercaptan is 3.9 percent.

Staff draft that is subject to change, approval, or disapproval by the Board.

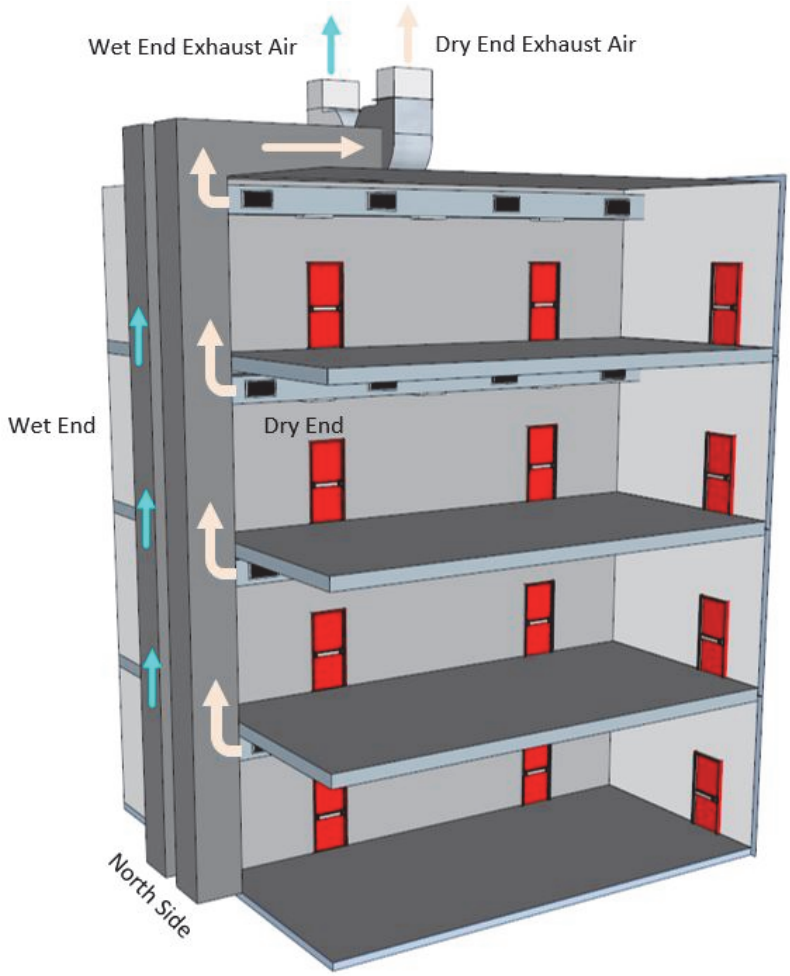

Figure 6. Simplified graphic cutout of the manufacturing building showing how the air dilution ventilation exhaust duct at each floor connects to the external vertical duct header and the roof mounted exhaust fans.

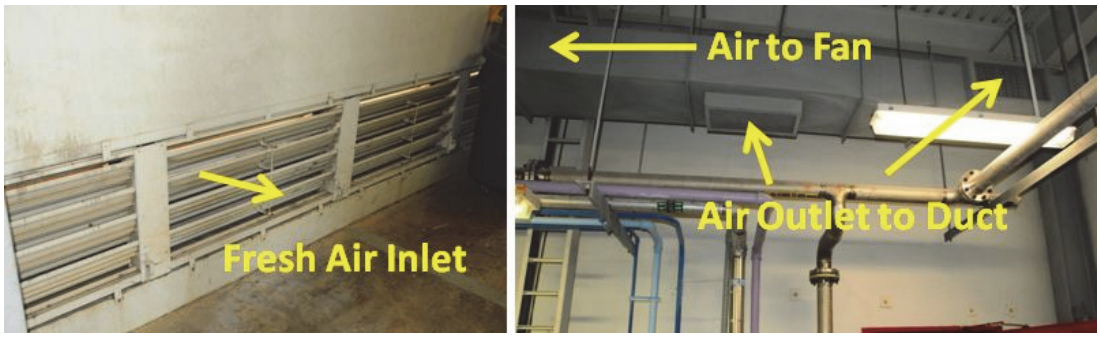

Figure 7. Typical air inlet louvers (left) and air outlet duct that exhausts the air towards the fans on the roof. The air louvers are located near the floor on the outside walls of each side of the manufacturing building and air is drawn to the center. The exhaust air ducts are located near the ceiling on the internal wall of each side of the manufacturing building.

Staff draft that is subject to change, approval, or disapproval by the Board.

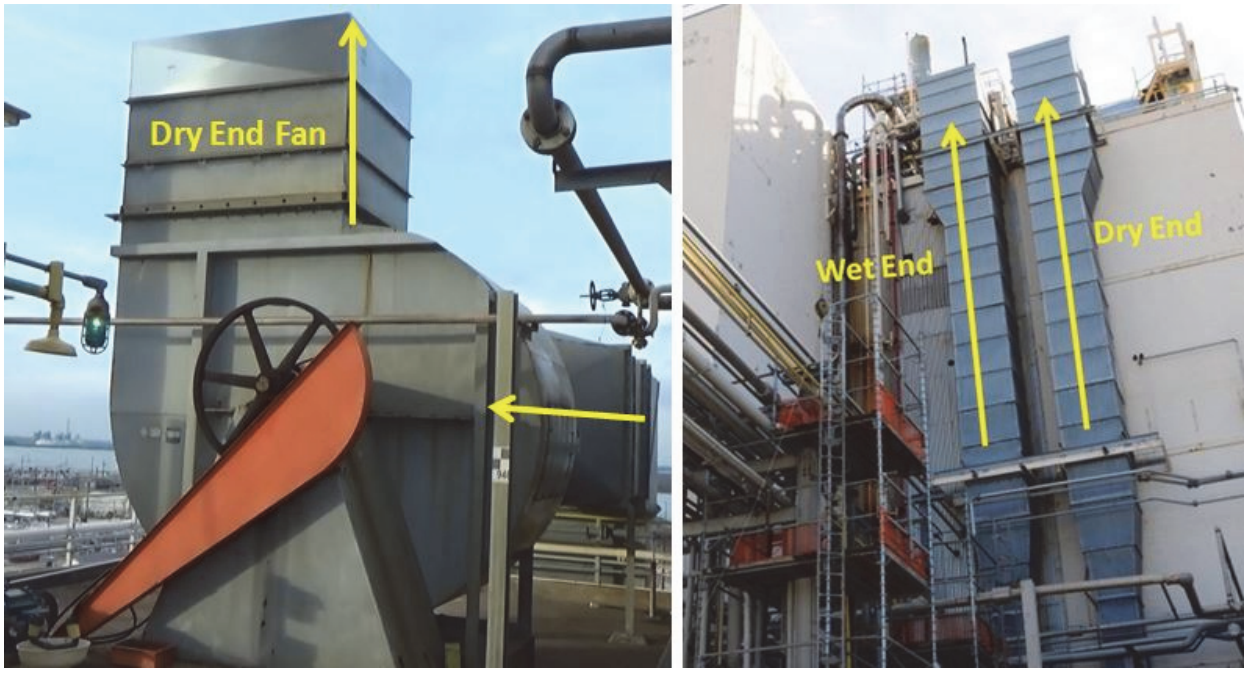

Figure 8. The dry end fan (left photo) and the exhaust air duct work (right photo). The exhaust air ducts from each floor are connected on the north side of the manufacturing building and air is pulled up through the fans and exhausted to atmosphere. Note – the dry end fan was not operational at the time this photo was taken.

Staff draft that is subject to change, approval, or disapproval by the Board.

Pre-Incident Activities

2011 Debottleneck and Emissions Reduction Project

10. In 2011, DuPont invested approximately 20 million dollars to implement a project to increase production rates and reduce environmental emissions for the IBU.[39] The key piece of equipment installed was the nitrogen oxides (NO_x) reduced scrubbed incinerator (NRS) shown in Figure 9.[40]

Figure 9. NRS Incinerator installed in 2011 to reduce emissions and allow increased production at the DuPont La Porte insecticide manufacturing facility.

[39] The DuPont Lannate® was a sold out product and DuPont was routinely looking for opportunities to increase capacity.
[40] The NOx (nitrogen oxides) reducing scrubbed (NRS) incinerator system is a vertical thermal oxidizer system for the destruction of organics, halogenated organics, and nitrogen-containing wastes with removal of acid gas from discharge.

Staff draft that is subject to change, approval, or disapproval by the Board.

11. The NRS Incinerator destroys process waste gas streams which are vented from equipment throughout the process. One of these waste gas streams contains methyl mercaptan vapor collected in a process vent system referred to as the waste gas vent header piping. This header originates from various Lannate® and API process vessels, from methyl mercaptan railcar unloading facilities, and from the methyl mercaptan storage tank. The waste gas vent header piping provides the path for these waste gas streams to be directed to the NRS Incinerator for thermal destruction (combustion).

12. Following the 2011 installation of the NRS Incinerator, DuPont experienced frequent high pressure events in equipment connected to the waste gas vent header piping.[41] DuPont determined one significant cause of these high pressure events was liquid accumulation in the vapor waste gas vent header piping.[42] The waste gas vent header piping to the NRS Incinerator was designed and installed in 2011without sufficient consideration of liquid accumulation. For example, it contained low points where liquid could accumulate, and there was no engineered equipment provided, such as a knock out drum,[43] to safely remove liquid from the waste gas vent header piping system.[44] Because some of the process vents contained water vapor, the common belief was that the accumulated liquid consisted primarily of condensed water with small amounts of other process chemicals, including methyl mercaptan.[45] As a result, to address high pressure events in the waste gas vent header piping operators were instructed to routinely open manual drain valves from the waste gas vent header piping to the atmosphere, directing the liquid towards floor drains located within the manufacturing building (Figure 10).[46]

---

[41] The high pressure in the waste gas vent header piping restricted vent sources flowing into the header, causing high pressure events in process equipment. These high pressure events could result in relief valves opening and discharging hazardous chemicals to the atmosphere.

[42] DuPont personnel believe the likely source of liquid accumulation was condensation from saturated vapor streams that originated in equipment operating above ambient temperatures. As these vapor streams entered the cooler waste gas vent header, liquid could condense and accumulate over time.

[43] A knock out drum is an industry term for a process vessel that provides for separation of vapor and liquid.

[44] The CSB identified three locations in the waste gas vent header piping to the NRS incinerator where liquid could accumulate: 1) inside manufacturing building (Figure 10); 2) the piping outside the manufacturing building as the piping passes through the MIC unit; and, 3) at detonation arresters just prior to where the waste gas from the waste gas vent header enters the NRS incinerator. Each location is equipped with a drain valve —two locations have atmospheric drains and only one location's drain is routed to a caustic scrubber.

[45] The liquid that was routinely drained from this system was never sampled and analyzed. Daily instructions—beginning April 14, 2014, and continuing until the incident—requested the operators to sample the unknown liquid. DuPont wanted a sample of the dark liquid reported for subsequent laboratory analysis to identify its chemical composition. This liquid was reported to have had a strong, noxious odor of sulfur compounds.

[46] DuPont never completed a management of change or established a formal procedure to drain liquid from the waste gas vent header. Rather, operators were directed to drain the system through written instructions in a daily instruction log book to operations staff. Beginning January 14, 2014, and continuing until the incident, the daily instructions required operators to drain the methyl mercaptan waste gas vent header "low point" on the 3rd floor once per shift by directing the liquid through a hose under a running safety shower until the liquid flow stops.

Staff draft that is subject to change, approval, or disapproval by the Board.

Figure 10. Waste gas vent header piping on the third floor of the manufacturing building. This portion, where several waste gas sources come together, is referred to as the waste gas vent header. Waste gas from this portion of the vent header travels up to reach the NRS Incinerator, a piping configuration that creates a low spot where liquid accumulates. To remove the liquid during waste gas vent header piping high pressure events, operators were instructed to open valves (yellow circle) and drain the system through a hose routed to a floor drain located near a safety shower. The floor drain is connected an open trench-type sump on the first floor. At the time of the incident, a second set of drain valves (red circle) were also opened directly to the floor inside the manufacturing building. This photo was taken while facing south. See Figure 11 for a view of the equipment while facing north.

Staff draft that is subject to change, approval, or disapproval by the Board.

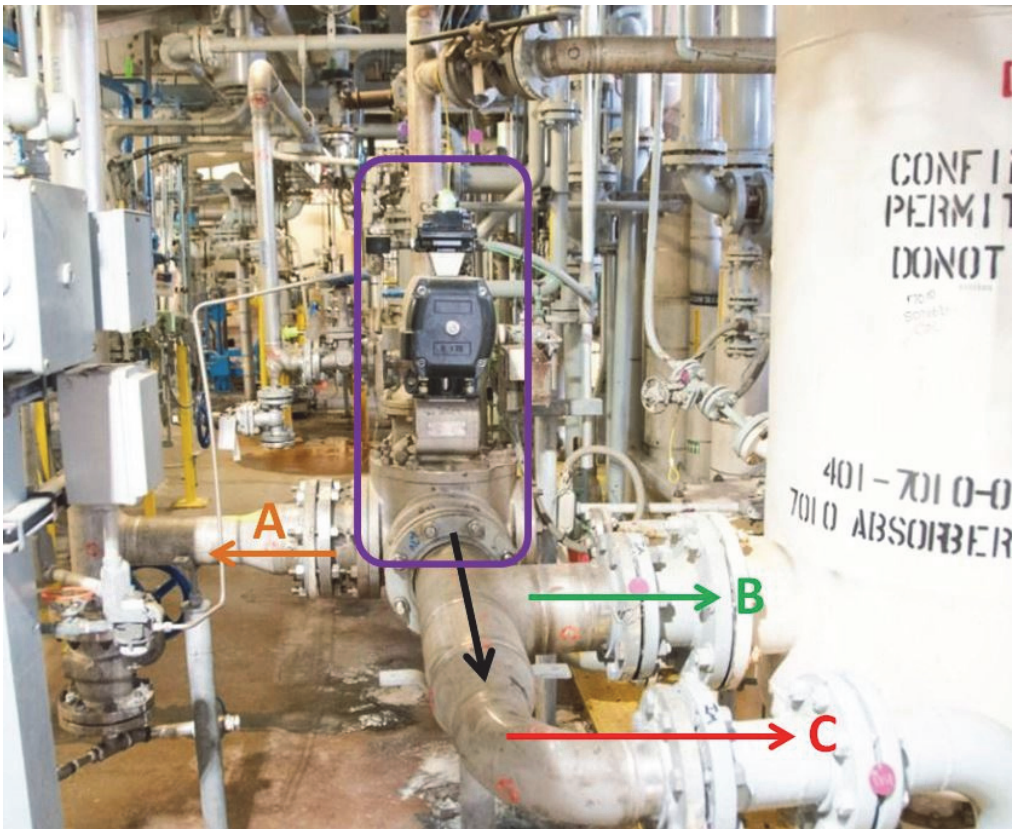

Figure 11. Waste gas vent header piping on the 3rd floor of the manufacturing building. This photograph was taken while facing north. Figure 10 shows the same waste gas vent header piping but taken while facing south. A 3-way valve (purple) is controlled to send the waste gas to either the NRS incinerator labeled "A" (orange) or a caustic scrubber labeled "B" (green). The caustic scrubber is designed with a vapor equalization line labeled "C" (red) that connects to the vapor space of the caustic receiver on the floor below (2nd floor). Prior to the installation of the NRS Incinerator, the 3-way valve did not exist and liquid that might accumulate in the waste gas vent header piping could freely drain into the caustic scrubber system.

Ventilation Fans Not In Service

13. Neither ventilation fan was operational at the time of the November 15, 2014 incident. The wet end fan and the dry end fan had poor reliability. The dry end fan had been down since June 2014, five months prior to the incident, due to an electrical problem. The wet end fan was shut down on October 20, 2014, because it was making a noise significant enough that DuPont operators turned it off and wrote an "urgent"[47] work order to have it repaired.

Unit Shutdown – Key Raw Material Diluted with Water

14. The incident chain of events began on Monday, November 10, 2014, with the unloading of an acetaldehyde oxime ("AAO") tank truck. AAO is a raw material for the Lannate® insecticide

[47] While the timing required to complete an "urgent" worker order is not specifically defined, based on CSB's review of DuPont records and interviews conducted with DuPont employees, it has a practical meaning of two to three days.

Staff draft that is subject to change, approval, or disapproval by the Board.

process. On Monday, during the unloading of an AAO tank truck, a water dilution system was inadvertently activated, and it continued to flow after the truck unloading was completed. Ultimately, the AAO storage tank overflowed.[48] The water diluted the normally 50 percent (%) AAO, 50% water mixture inside the tank to approximately 24% AAO, which is outside of normal parameters. The diluted AAO caused operating difficulties that forced a shutdown of the Lannate® insecticide process.

Startup Attempted – Plugging Identified in Reaction System

15. Modifications to the AAO concentration control system were made to address the diluted AAO. On Wednesday, November 12, 2014, DuPont operators attempted to restart the Lannate® process. However, during the shutdown, the methyl mercaptan reaction section, which generates a salt-slurry material, had plugged (Figure 12), and flow could not be established to accomplish the restart.

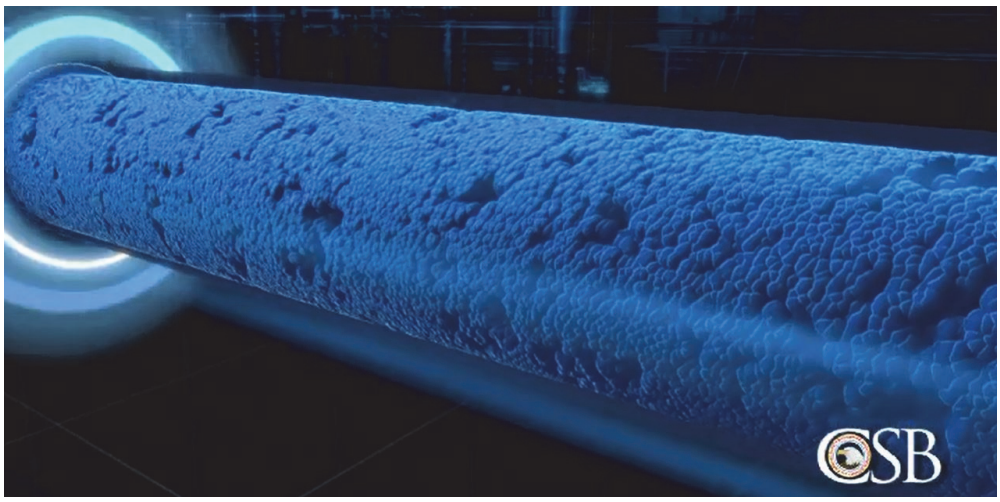

Figure 12. Snippet from CSB animation depicting the salt-slurry plugging within the methyl mercaptan reaction system.

16. Plugging of the equipment by the salt-slurry material following a shutdown is common. However, even though routine practices existed there were no written procedures for how to clear the reaction system. To clear the system, operators put hot water both outside and inside of the equipment, a historical site practice that typically clears the plug. Eventually, the salt-slurry

[48] During the AAO truck unloading, a block valve downstream of what should have been an out-of-service water dilution control valve was inadvertently opened, allowing water to flow into the tank. The water dilution system had been installed in 2006 when container shipments of 100% AAO were judged to be more economical. AAO is now typically purchased and stored as a 50% solution with water. A logistical problem resulted in an unusual delivery of 50% AAO by tank truck instead of by railcar. Two factors contributed to the tank overflow incident. First, DuPont did not have a procedure for unloading a 50% tank truck of AAO. In addition, the AAO water dilution control valve was supposed to interlock closed when: 1) the truck unloading pump was off; or, 2) when the AAO tank had a high liquid level. However, the interlock function had been bypassed in the field so that water could be used to decontaminate the tank during the turnaround in spring 2014. Instrument air supply tubing was connected directly to the interlock valve actuator, bypassing the interlock activation solenoid, and forcing the valve to remain fully open. The interlock could not function because the bypass was not removed at the completion of the turnaround.

Staff draft that is subject to change, approval, or disapproval by the Board.

material within the methyl mercaptan reaction system was cleared and another startup was attempted. However, this startup attempt also failed because flow of methyl mercaptan could not be established. Although the reaction section was now clear, there was additional plugging located in the methyl mercaptan feed line between the methyl mercaptan storage tank and the reaction system. DuPont personnel have stated to the CSB that plugging in this area had never previously occurred. Unlike the reaction system routine practices were never established to clear the methyl mercaptan feed line. Similar to the reaction system, DuPont written procedures were not developed to clear the methyl mercaptan feed line.

Water Inadvertently Added to Methyl Mercaptan—Forms Hydrate Blockage

17. A review of process data revealed that on Wednesday night (November 12, 2014), the level in the methyl mercaptan storage tank (Figure 13) rose approximately 2%. Approximately 2,000 pounds of water had likely been inadvertently sent to the methyl mercaptan storage tank as a result of the operational activities that took place during attempts to clear process equipment plugging in the reactor system fed from the upstream methyl mercaptan storage tank.[49] This tank level rise was not noticed at the time.[50] The methyl mercaptan storage tank and the feed line to the reaction system now contained a mixture of methyl mercaptan and water.

18. Water combining with methyl mercaptan does not normally create a hazard. However, at low temperatures (≤ 52 °F) water and methyl mercaptan form a solid, ice-like material commonly referred to as a "hydrate."[51] Temperatures in the Houston area for the 24 hours preceding the incident averaged approximately 40 °F and had been consistently below 55 °F since Tuesday, November 11, 2014. Formation of a hydrate in the methyl mercaptan feed system caused the unusual plugging and inability to initiate feed of methyl mercaptan to the reaction system. At this time, DuPont operations personnel were unaware of the back-flow of water into the methyl mercaptan storage tank. Nor did they realize that the methyl mercaptan feed system was contaminated with water and that hydrate was the source of the plugging. To resume production, DuPont would need to warm the contents of the feed system in order to dissociate (melt) the solid hydrate material back to a liquid mixture of water and methyl mercaptan.[52]

---

[49] The water source was located downstream of the methyl mercaptan storage tank and entered the system from the reverse of its normal flow path.

[50] Because the initial tank level was already high, the addition of nearly 2,000 pounds of water was sufficient to trigger a high level alarm at 9:56:03 pm and an emergency high level alarm at 11:28:21 pm on November 12, 2014. However, these alarms were not acknowledged until 5:42:44 am on November 13, 2014.

[51] DuPont personnel commonly refer to the methyl mercaptan clathrate hydrate simply as a "hydrate." The clathrate hydrate dissociates at approximately 52 °F. See Mohammadi, Amir H., and Richon, Dominique, 2011. "Equilibrium Data of Sulfur Dioxide and Methyl Mercaptan Clathrate Hydrates," Journal of Chemical & Engineering Data, 2011, Vol. 56, pp. 1666–1668.

[52] Although the methyl mercaptan hydrate with water had been identified in DuPont's methyl mercaptan technical standard and in PHAs years earlier, DuPont never implemented safeguards, such as heat tracing, or developed a procedure to safely dissociate the hydrate.

Staff draft that is subject to change, approval, or disapproval by the Board.

Figure 13. The yellow box outlines the 18,000 gallon methyl mercaptan storage tank at the DuPont facility in La Porte, Texas. Both the Lannate® and Vydate® insecticide processes use methyl mercaptan as a key raw material.

Activities During the Shift Before the Incident

19. Two significant changes occurred on Friday morning (November 14, 2014). The first change was the start of a different group of operations personnel on shift. Most had not been at the site since before the AAO tank dilution and overflow incident had occurred and they were learning of the situation for the first time. They were unaware of the required shutdown and of the difficulties with reaction system plugging and the plugging of the methyl mercaptan feed system. The second change was the initial concerted involvement of a DuPont Technical Team of managers and engineers in the methyl mercaptan feed system troubleshooting activities. During the morning, unit engineers and managers (DuPont Technical Team) met as a group with the day shift supervisor to discuss the methyl mercaptan plugging problem and to develop a plan to clear the piping so that both the Lannate® and the API processes could be restarted. This meeting identified the likely scenario that water had entered the methyl mercaptan system and a solid hydrate was developed. DuPont's methyl mercaptan technical standard identifies the potential formation of a hydrate at low temperatures. The technical standard states, "[methyl mercaptan] will form a hydrate with water, which is a solid below 40 deg F per information provided by a [methyl mercaptan] supplier." Based on this understanding, the DuPont Technical Team requested that operators put hot water on the outside of the methyl mercaptan feed piping, under the insulation, to warm the piping and its contents to dissociate the hydrate back to liquid methyl mercaptan and water (Figure 14).

Staff draft that is subject to change, approval, or disapproval by the Board.

Figure 14. Hot water hose positioned on the liquid methyl mercaptan feed piping to flow hot water between the piping and the insulation in an effort to heat the piping and dissociate the solid hydrate that formed after water inadvertently entered the mercaptan storage tank.

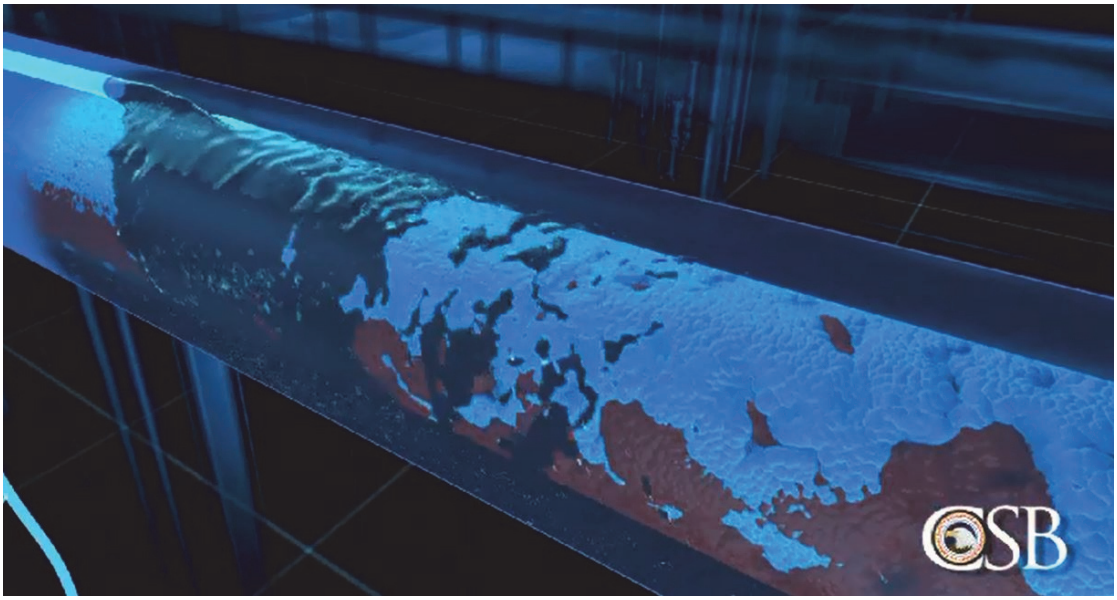

Figure 15. Snippet from CSB animation depicting DuPont's use of hot water hoses placed under the insulation to provide heat to dissociate the hydrate back to methyl mercaptan and water.

20. The DuPont Technical Team realized that when heated methyl mercaptan would expand and would need a safe place to vent to avoid overpressure of the feed line. To address this concern, DuPont operations personnel opened valves between the methyl mercaptan feed line and the waste gas vent header. Along the methyl mercaptan feed line there were three locations where it was connected by valves to the waste gas vent header— piping intended to remove excess or unwanted vapor from the process and route it to the NRS incinerator for thermal destruction. DuPont personnel used pressure gauges at those three valves (Figure 16) to determine where the blockage was, and what progress they were making to clear it. At the time of the incident, one of

Staff draft that is subject to change, approval, or disapproval by the Board.

these three valves between the methyl mercaptan feed system and the waste gas vent header was fully open. A second valve was slightly open.

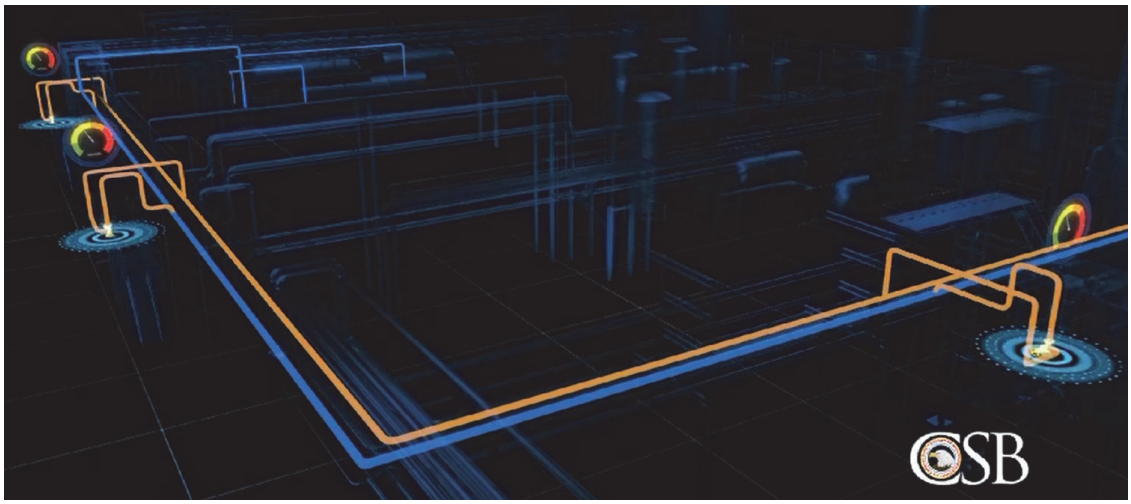

Figure 16. Snippet from CSB animation depicting the three locations where valves connected the methyl mercaptan feed line (blue) to the waste gas vent header (orange) piping. Pressure gauges shown at these locations were used to monitor the progress of clearing the hydrate blockage inside the methyl mercaptan feed line.

21. Although required by EPA's Risk Management Plan (RMP)[53] rule, OSHA's Process Safety Management (PSM)[54] standard, and their own company standards, DuPont did not develop written procedures, conduct any type of hazard analysis for abnormal conditions, carry out a job safety analysis, perform a management of change, nor conduct any other type of hazard analysis prior to implementing the plan the DuPont Technical Team developed that morning. For example, there was no systematic safety review of the use of the valves connecting the methyl mercaptan feed line to the waste gas vent header. Additionally, there was no development of a written procedure to guide operations or to track success of the plan or progress toward clearing the entire methyl mercaptan feed system.

22. DuPont management relied upon verbal communication of the plan to the day shift supervisor. At the end of the day shift, DuPont relied on the face-to-face verbal communication between shift supervisors to transition the efforts to the night shift. This night shift supervisor was learning of the shutdown and subsequent startup difficulties for the first time.[55] Although the DuPont Technical Team verbally communicated with the day shift supervisor, the Team did not meet with the newly-involved night shift supervisor nor did they communicate verbally or in writing with the night shift operations personnel. In addition, DuPont did not provide on-site technical (engineering) personnel to support the night shift.[56]

[53] EPA Risk Management Plan, U.S.C. Section 42, Chapter 85, Subchapter I, Part A, Section 7412(r).
[54] OSHA Process Safety Management of Highly Hazardous Chemicals Standard, 29 CFR §1910.119.
[55] The only written communication to the night shift supervisor was a note in the shift log that stated "Unplugging M[e]SH Header." MeSH is DuPont's abbreviation for methyl mercaptan.
[56] DuPont technical personnel are routinely on call to provide support.

Staff draft that is subject to change, approval, or disapproval by the Board.

23. The DuPont operations day shift began implementing the plan that the DuPont Technical Team developed by applying hot water under the insulation and on the outside of the liquid methyl mercaptan piping.[57] DuPont operators started this process at the methyl mercaptan storage tank and the associated methyl mercaptan feed pump piping segments, and then worked their way down the methyl mercaptan feed line towards the reaction system. Pressure gauges at each of the three block valves between the liquid methyl mercaptan feed line and the vapor waste gas vent header piping system were used to determine the success and progress of the work. Using these valves in this way followed the plan developed by the DuPont Technical Team. However, this alignment created a direct path between the feed system and the waste gas vent header, which was outside of DuPont's design intent. It had not been effectively evaluated under DuPont's process safety management systems.

The Incident

24. After shift change, the night shift continued implementing the plan that was developed earlier that day by the DuPont Technical Team. Initially, the night shift operations personnel determined that some of the piping at the methyl mercaptan storage tank was either still plugged or had plugged again. They began their activities by working to clear this section. They applied hot water to the outside of the liquid methyl mercaptan piping steadily working their way towards the reaction system.

25. Eventually, DuPont operations personnel tested to determine if they could establish methyl mercaptan flow to the reaction system. The methyl mercaptan pump to Lannate® was in operation and circulation back to the tank was established. However, when they attempted to feed forward to the reaction system they could not establish methyl mercaptan flow. DuPont operations staff concluded that too much hydrate plugging remained, and at approximately 1:30 am on Saturday (November 15, 2014), they temporarily halted troubleshooting and went back to the control room to take a break and discuss how to proceed. During their break, the pump remained on circulating methyl mercaptan and the hot water was still heating the methyl mercaptan piping. Additionally, one of the valves between the liquid methyl mercaptan feed line and the waste gas vent header piping was cracked open and a second valve was fully open (Figure 17).

[57] Applying hot water to the outside of the methyl mercaptan liquid piping system was outside of the design considerations for the thermal expansion relief valve on this system. As previously stated, DuPont did not perform management of change prior to instructing operations personnel to use the hot water. DuPont Standards, as well as the EPA RMP and OSHA PSM regulations, required DuPont personnel to conduct a management of change review.

Staff draft that is subject to change, approval, or disapproval by the Board.

Figure 17. The fully open valve (left photo) and the cracked open valve (right photo) between the methyl mercaptan feed line and the waste gas vent header. These post-incident photos show the valve positions at the time of the incident.

26. A post-incident evaluation of process data identified that the level in the methyl mercaptan storage tank began to drop at approximately 2:45 am. Liquid methyl mercaptan had started to flow into the waste gas vent header piping (Figure 18). This was likely caused by the hydrate being dissociated sufficiently to allow liquid to flow forward and through the connections opened between the liquid methyl mercaptan piping and the waste gas vent header piping. However, the drop in methyl mercaptan storage tank level was not detected, because the level was still within normal operating limits.

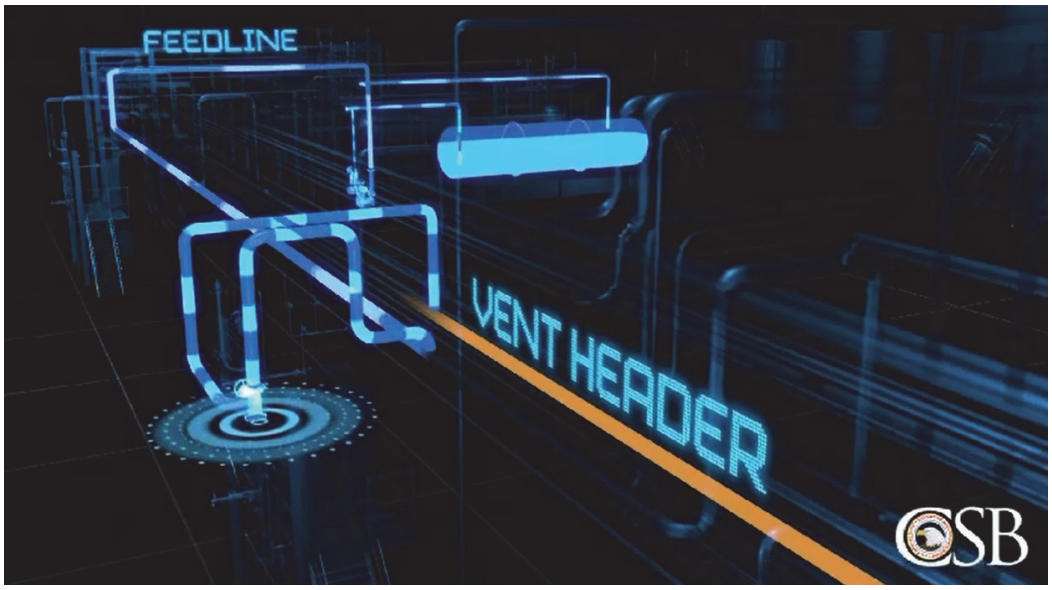

Figure 18. Snippet from CSB animation depicting the piping arrangement that allowed liquid methyl mercaptan from the feed line (blue) to flow into the waste gas vent header piping (orange).

Staff draft that is subject to change, approval, or disapproval by the Board.

27. DuPont operations personnel who had gone into the control room (Figure 19) were not aware that the level in the methyl mercaptan storage tank was decreasing. The methyl mercaptan being fed to the system by the pump followed the path of least resistance through the opened valve into the waste gas vent header piping. The presence of methyl mercaptan in the vent header began to cause high pressure in the waste gas vent header. Operations personnel became aware of the high pressure when other insecticide manufacturing equipment venting into the waste gas vent header began to exhibit high pressure alarms. At this point, operations personnel shifted their attention from the problem of plugging in the methyl mercaptan feed system to the current problem of high pressure in the waste gas vent header piping to the NRS Incinerator. Recall that high pressure events in the waste gas vent header piping to the NRS Incinerator had been a relatively common problem since the NRS Incinerator was installed in 2011.

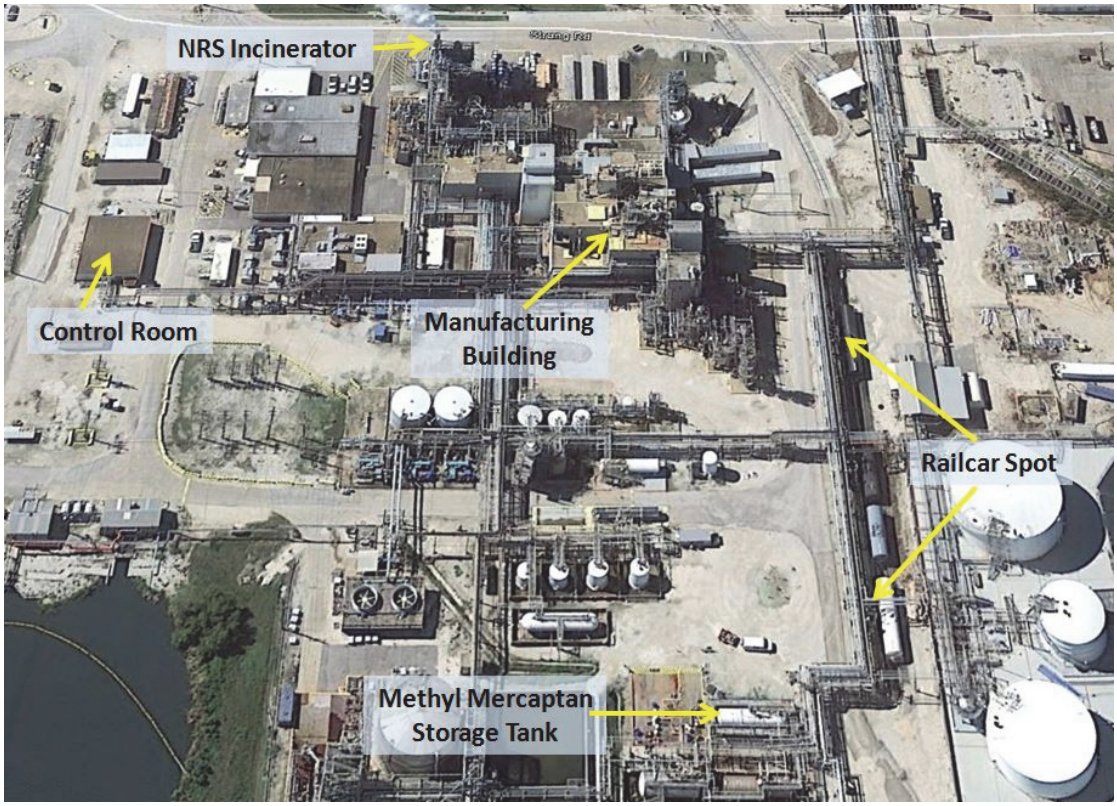

Figure 19. Overhead photo of the DuPont La Porte IBU showing the location of the control room, manufacturing building, railcar spots, and methyl mercaptan storage tank.

28. On the night of the incident, DuPont operations staff did not correlate the high pressure problem with the unusual activities (hydrate dissociation) surrounding the plugging of the methyl mercaptan feed line. Rather, they attributed the high pressure event to the routine problem of liquid accumulation in the waste gas vent header piping. They responded to the high pressure with the routine line draining practices that had been successful in the past. Normally when operations personnel opened the valves shown in Figure 10 a dark liquid with a strong sulfurous

Staff draft that is subject to change, approval, or disapproval by the Board.

odor would drain. However, this time a nearly pure stream of highly toxic and highly flammable methyl mercaptan was released filling the room with vapor where there was no active mechanical air dilution ventilation.

Distress Call

29. Approximately fifteen minutes after the DuPont operations personnel (Shift Supervisor and Operator 1) separately went to drain the waste gas vent header piping, Operator 1 made an urgent call over the radio for help. From the tone and urgency of the message, it was obviously an emergency situation; however, the nature and location of the emergency were not effectively communicated.[58]

30. After hearing the distress call, the control room operator tried to get more information through radio communication, but neither of the workers in the building responded. Two other operators (Operator 2 and Operator 3) in the control room then ran to the manufacturing building to respond to the distress call. Another operator (Operator 4), who was outside, saw Operator 2 and Operator 3 running into the building and followed them. These three operators did not realize they were responding to a dangerous, highly toxic, and highly flammable gas release. They did not wear or take with them any respiratory personal protective equipment (PPE).

31. Simultaneous to the distress call, an operator (Operator 5) working on the first floor of the manufacturing building began to feel dizzy and to have blurry vision. Operator 5 realized he was in trouble and managed to exit the building where he immediately fell to the ground. Shortly after he had fresh air to breathe, he began to recover.

32. The three operators (Operators 2, 3, and 4), who responded to the distress call by Operator 1, acted separately and all took different routes into the manufacturing building. Operator 2 entered the south stairway and likely went directly to the third floor where he was fatally overcome by methyl mercaptan. Operator 3 thought the distress call indicated the problem was on the fourth floor, so he ran up the south stairway to the fourth floor but could not find anyone. Operator 3 did not have a radio, so he called on the IBU public address system and stated that he did not see anyone on the fourth floor. The control room operator told him to check the third floor, but Operator 3 began to feel light-headed. He made his way back into the south stairway, but was overcome by the methyl mercaptan exposure. Operator 3 lost consciousness while descending the stairs from the fourth floor, bumping his head and breaking his glasses when he fell. Operator 3 regained consciousness about 45 minutes later and managed to exit the building on his own volition. He was subsequently transported to the hospital when emergency responders observed he was disoriented from his exposure. Operator 4 entered the process portion within the manufacturing building from the south stairway onto the second floor. He walked about ten feet into the manufacturing building and hit what he described as a "wall" of methyl mercaptan. He

[58] Some DuPont personnel who heard the distress call informed the CSB that they interpreted the urgent communication to indicate that Operator 1 had a personal injury, such as a broken leg. They were not aware of the highly toxic methyl mercaptan leak.

Staff draft that is subject to change, approval, or disapproval by the Board.

began to feel woozy, light headed, and nauseated, but managed to retreat back to the south stairway.

33. Except for the initial public address call from Operator 3, the Lannate® control room operator could not get any responses on the public address system or by radio from either the original two workers in the building or any of the three operators. After the lack of response from the field operators, another board operator (Operator 6), who was the brother of Operator 2, began to prepare to head to the building. Other operators in the control room told him not to enter the building because of the unknown severity of the situation. However, Operator 6 headed toward the manufacturing building, taking three five-minute emergency escape air bottles (Figure 20).

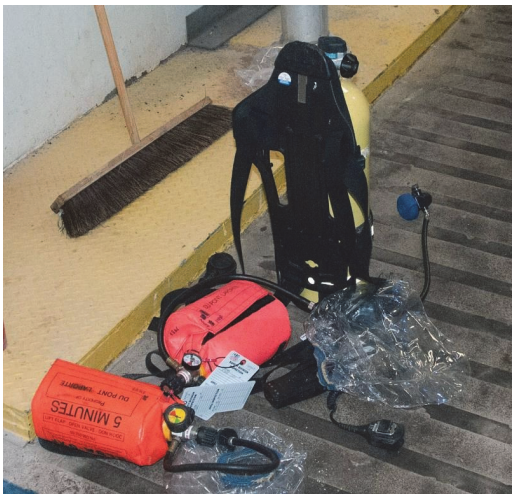

Figure 20. Photo of the 5-minute escape air bottles and 30-minute self-contained breathing apparatus (SCBA) on the third floor, dry end (west) side of the manufacturing building following the incident. The third 5-minute escape air bottle was put on Operator 4 and was left at the control room entrance. The 30-minute SCBA was originally just outside the door to the third floor entrance at the south stairway. It is presumed that Operator 6 grabbed this SCBA prior to entering the third floor.

34. Entering the south stairway, Operator 6 encountered Operator 4 disoriented from the exposure that had occurred on the second floor. Operator 6 put an escape air bag over the head of Operator 4 and opened the valve on the escape air bottle. Operator 6 put the second of the three escape air bags on himself, opened the valve to his air bottle, and continued up the stairs to the third floor. With the aid of the fresh air escape pack, Operator 4's symptoms improved, and he was able to exit the building safely.

35. The Lannate® control room operator called for the plant emergency response team (ERT) to respond. The ERT originally believed they were responding to a rescue situation such as an injury, not a highly toxic and highly flammable chemical release. As a result, they arrived with rescue equipment, but did not have adequate personal protective equipment (PPE) to enter the building. About an hour and a half after the initial distress call, the ERT obtained appropriate PPE and was able to make an initial entry into the manufacturing building.

Staff draft that is subject to change, approval, or disapproval by the Board.

36. The Shift Supervisor, Operator 1, Operator 2, and Operator 6 were all located by emergency responders, but none were responsive. The drain valves from the waste gas vent header on the third floor (Figure 10) were found open with methyl mercaptan flowing from them. The Shift Supervisor was located on the third floor approximately 30 feet north of the drain valves. Operator 1 was located in the north stairway. It appeared that Operator 1 had succumbed before reaching the second floor while descending from the third floor. Emergency responders found Operator 6 next to his brother (Operator 2) on the dry end side of the building. Operator 2 had the third of the escape air bags brought by Operator 6 on his head. Operator 6 had a self-contained breathing apparatus (SCBA) 30-minute air bottle in front of him and the mask on his face, but he had not connected the mask to the air bottle. It is likely that Operator 6 had entered the third floor and when he found Operator 2 down he put the third escape air bag over Operator 2's head. When his own escape pack began to run out of air, Operator 6 tried to put on an SCBA that was located on the third floor. However, it appears that Operator 6 was fatally overcome from methyl mercaptan before he could connect his breathing air mask to the SCBA.

Key Findings

Not Applying Inherently Safer Design Lessons More Broadly

37. DuPont did not effectively control worker exposure to highly toxic chemical and asphyxiation hazards inside the manufacturing building despite the similar process safety hazards DuPont addressed following the Bhopal methyl isocyanate (MIC) incident in 1984.[59] After Bhopal, DuPont made major technology changes to the MIC process at La Porte that focused on inherently safer design. DuPont approved the MIC project on January 30, 1985, and completed construction on the high-priority, expedited project only four months later on April 30, 1985. The inherently safer design improvements included moving the MIC processing equipment outside of the manufacturing building and using an outdoor open structure design to eliminate the need for dilution air ventilation (Figure 21). In addition, unlike the Lannate® and API processing equipment that contain highly toxic materials, such as methyl mercaptan and chlorine, pressure relief systems on equipment containing highly toxic MIC are routed to an incinerator for destruction.

- Minimum in-process hold-up of MIC
- Minimum process piping runs and number of flanges
- Relief devices with MIC vented to an incinerator abatement
- Use of an open building structure with potential leak sources shrouded and vented to the incinerator
- Lethal service equipment and piping design
- Immediate consumption of MIC in the methomyl/oxamyl reactors to minimize inventory of MIC
- Multi-layer interlock systems for fail safe operation.

[59] DuPont standards identify methyl isocyanate, methyl mercaptan, and chlorine as highly toxic materials (HTM). "[…] [The HTM standard] is intended to focus on materials that are highly toxic and highly volatile, such that they pose significant acute exposure risks to people off-site if accidentally released. Acute exposure, in this context, involves potentially life-threatening health effects resulting from up to a 60-minute exposure period."

Staff draft that is subject to change, approval, or disapproval by the Board.

Figure 21. DuPont moved its MIC process equipment to an open structure design (outside of the manufacturing building) after the 1984 Bhopal incident. DuPont documents identify this as an inherently safer approach.

38. DuPont's process safety programs support inherently safer design (ISD) and require that inherently safer design principles be applied. DuPont's corporate standard for process hazard analysis states:

> *Inherently safer technology (IST) should be applied where it reduces process hazards and makes good sense.*
>
> *Processes are made inherently safer through the elimination of hazards rather than their control. As a result, the use of ISP [inherently safer process] technology sometimes referred to as inherently safer technology or IST is an approach to the safe design and operation of facilities.*
>
> *PHAs include the activities of hazard identification, consequence analysis, hazards evaluation, interlock evaluation, human factors evaluation, facility evaluation, inherently safer process (ISP) evaluation, and development of recommendations.*
>
> *Opportunities for making a process inherently safer can be identified at any time during the life cycle of the process. Project and cyclical PHAs typically provide such opportunities and they should be capitalized to the greatest extent possible.*
>
> *Cyclic [PHA] reviews shall review the existing process in an effort to identify further opportunities for the application of ISP [inherently safer process] concepts in either the current process or a future generation of the process.*

Consequently, DuPont's process safety programs require that inherently safer design principles, such as the open building of MIC, be applied to all processes "to the greatest extent possible."

39. The portion of the manufacturing building where the incident took place does not have a design purpose, yet housing the process equipment inside the enclosed manufacturing building exposed personnel to highly toxic chemical exposure and asphyxiation hazards that DuPont has not effectively identified or controlled. For example, DuPont has never performed a PHA on the building ventilation system. In addition, DuPont PHAs identify that the enclosed manufacturing building creates hazards, such as flammability, toxic exposure, and asphyxiation. However, these same PHAs do not claim that benefits are provided by enclosing the process equipment in a building. The manufacturing building is never used as a safeguard in a DuPont PHA. After reviewing technical documents and interviewing DuPont technical staff, the CSB learned that the chemical processing taking place on the wet and dry end in this area does not require the vast

Staff draft that is subject to change, approval, or disapproval by the Board.

majority of this equipment to be located inside a building.[60] DuPont could eliminate these hazards to workers by using the inherently safer design approach applied to the MIC process and locating this equipment outside of an enclosed structure.

40. The recognized safety tradeoff with toxic chemical containment buildings is that, while they reduce risk to the community, they trap and concentrate material from leaks inside the building, increasing risk to personnel.[61] The DuPont manufacturing building was not designed as a containment building. As a result, it introduces all of the increased personnel hazards of a containment building, but offers none of the beneficial off-site risk reduction for the community. The DuPont manufacturing building has the same increased risk to personnel that a containment building has—toxic leaks are trapped and concentrated inside the building. Furthermore, the DuPont manufacturing building is not designed to limit the impact of a toxic chemical leak off-site by containing the leak and routing it to a destruction device such as an incinerator or scrubber. Instead, the manufacturing building ventilation air exits the fans on the roof of the building directly to atmosphere. With no additional destruction device, the manufacturing building does not decrease risk of chemical exposure to the public.[62,63]

41. The ventilation design for the manufacturing building does not take into consideration toxic chemical exposure hazards even though the building contains two highly toxic materials, chlorine and methyl mercaptan.[64] DuPont records indicate that the dilution air ventilation design is based on providing sufficient ventilation to ensure that the concentration of flammable gases does not exceed 25 percent of the lower explosion limit (LEL).[65] However, there are no LEL detectors for the manufacturing building to monitor the atmospheric conditions and alert workers of potential fire or explosion conditions. Furthermore, a methyl mercaptan concentration of 25 percent of the LEL is equivalent to 65 times the IDLH.[66]

---

[60] The packaging area of the building on the ground floor (west side) may have a legitimate need to be inside a building. Dust control and keeping the packaging equipment and methomyl product dry appear to be important considerations that may justify keeping packaging area equipment housed inside a building.
[61] See Center for Chemical Process Safety (CCPS). "Inherently Safer Chemical Processes – A Life Cycle Approach." 2009; pg 58-59.
[62] Ibid.
[63] The DuPont corporate PHA standard references this same CCPS publication (Inherently Safer Chemical Processes – A Life Cycle Approach) when discussing how to approach making processes inherently safer.
[64] DuPont's design objective for the ventilation system states, "The main objectives of industrial ventilation for the LANNATE®/API manufacturing building are to: a. control contaminants to acceptable work place exposure levels, e.g. comply with OSHA regulation or Corporate AELs (acceptable exposure limits), and b. prevent fires and explosions." However, the actual design calculations do not take toxics into consideration. In addition, DuPont has not established an AEL for methyl mercaptan.
[65] DuPont records indicate that the manufacturing building ventilation system design code is NFPA 497, Recommended Practice for the Classification of Flammable Liquids, Gases, or Vapors and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas. NFPA 497 defines adequate ventilation as that sufficient to ensure that the concentration of flammable gases does not exceed 25 percent of the lower explosion limit (LEL).
[66] The IDLH for methyl mercaptan is 150 parts per million (ppm). See http://www.cdc.gov/niosh/idlh/74931.html (accessed July 8, 2015). According to OSHA, "Immediately dangerous to life or health (IDLH) means an atmosphere that poses an immediate threat to life, would cause irreversible adverse health effects, or would impair an individual's ability to escape from a dangerous atmosphere." See https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=12716 (accessed July 8, 2015).

Staff draft that is subject to change, approval, or disapproval by the Board.

42. The DuPont manufacturing building does not have adequate dilution air ventilation or sufficient air monitoring to ensure the safety of workers. There are multiple potential inhalation hazards inside the building including nitrogen, and the highly toxic materials chlorine and methyl mercaptan. To ensure protection from these hazards, CSB investigators only entered the building while accompanied by a contracted industrial hygienist performing continuous air monitoring, and only while wearing air-purifying respirators and carrying 5-minute escape bottles. All CSB investigator building entries began with a trip to the roof of the building to visually verify that the ventilation fans were in operation before continuing. DuPont employees do not follow a similar safety protocol.

43. CSB interviews revealed that key DuPont technical personnel were not aware of basic details of the building ventilation design, such as air flow direction. In addition, a technical operations supervisor was unaware of their responsibility for the operation of the "PSM Critical"[67] ventilation equipment.

44. Although DuPont mechanical integrity procedures call for annual air flow testing, the manufacturing building ventilation system for the immediate area impacted by the methyl mercaptan release (the wet end fan) had never been tested for flow rate or effective distribution of dilution air. A 2009 audit of the DuPont La Porte's PSM system found that the ventilation system was not being tested. The audit created an action item to fill this gap. All that was required to close the associated audit action item was to create a program that periodically generated a work order to conduct dilution air flow testing. The action item was closed in 2010 without this testing ever taking place. In 2012, it was identified that testing had not occurred. Because DuPont technical personnel did not understand the testing requirements, the ventilation system was not fully evaluated. Despite the 2009 audit finding, the flow rate and effective distribution of dilution air for the wet end fan was never tested. Moreover, only dilution air flow measurements for the dry end fan were taken, but there was no analysis—just measurements.

45. The manufacturing building ventilation fans were classified as "PSM Critical" equipment by DuPont. DuPont recognized that a ventilation fan breakdown could result in a high consequence event. However, neither the wet end fan nor the dry end fan was in operation at the time of the incident. Preliminary calculations indicate that even with both fans operating, ventilation as it existed would likely have been insufficient to reduce the lethal concentration of methyl mercaptan and prevent the death of the Shift Supervisor and Operator 1.

46. Following a 1971 hazard review, DuPont installed alarms on the manufacturing building ventilation fans so operations personnel would be notified if a ventilation fan stopped operating. DuPont also added a daily inspection to the operator checklist. While the daily inspection is still being performed, at the time of the November 15, 2014 incident there was no longer an alarm to notify operators that the fan was not running. CSB investigators learned that the alarm was

[67] DuPont assigns the designation of PSM Critical to equipment whose failure could result in a high consequence event.

Staff draft that is subject to change, approval, or disapproval by the Board.

eliminated in the mid-1990s when the facility upgraded the pneumatic panel board controls and installed a computer-based distributed control system (DCS). [68]

47. At the time of the incident, the manufacturing building ventilation fans for the portion of the unit where the methyl mercaptan was released were not operating despite being classified as "PSM critical," and despite being the subject of an "urgent" work order written nearly a month earlier, on October 20, 2014.

48. DuPont La Porte procedures require that worker access to the building be "restricted" when any of the ventilation fans are not in service (Figure 22). However, the breakdown of the ventilation fans did not result in any additional restrictions or safety precautions, such as extra personal protective equipment (PPE) requirements, worker access restrictions to the manufacturing building, or supplemental operational or emergency response protocols. The poor reliability of the fans had been normalized[69] to the point where building access was no different with the fans running than with the fans off.

4. Emergency Procedures

In the event of a power failure, building ventilation will be lost. As soon as a power resumes, it is important to restart the ventilation fans using the field switches located on the roof near each fan.

Repair of the fans must have high priority. The fans are listed as critical equipment in the maintenance system. While a building ventilation fan is out of service, work, material, and people access to the affected area is restricted.

Figure 22. DuPont emergency procedures call for access to the building to be restricted if a ventilation fan is out of service. However, the actual practice for building access was no different with a fan out of service than if all the fans were operating.

49. Analyzer houses in the MIC process area outside of the manufacturing building are equipped with oxygen analyzers and lights that warn potential entrants if the internal atmosphere is low in oxygen concentration and not safe to enter (Figure 23). However, the manufacturing building has no similar oxygen atmosphere monitoring or warning system despite having significantly larger inventories of hazardous chemicals and unventilated areas.

[68] DuPont plans to provide an alarm to indicate when a ventilation fan is not operating prior to resuming insecticide manufacturing operations at the La Porte facility.

[69] Normalization of deviance is a long-term phenomenon in which individuals or work teams gradually accept a lower standard of performance until the lower standard becomes the norm. It is typically the result of conditions slowly changing and eroding over time. See Center for Chemical Process Safety (CCPS), "Recognizing Catastrophic Incident Warning Signs in the Process Industries." 2012; pg 4.

Staff draft that is subject to change, approval, or disapproval by the Board.

Figure 23. Unlike the manufacturing building this DuPont analyzer house shown in the left photo is equipped with safeguards to ensure entrant safety. The oxygen analyzer shown in the right photo is inside the analyzer house continuously monitoring the analyzer house atmosphere. If a nitrogen leak occurs inside the analyzer house sufficient enough to cause the atmosphere inside to approach dangerous levels, an alarm sounds and the green light outside the door turns off to indicate it is not safe to enter. The manufacturing building lacks similar safeguards. The CSB has not been able to determine why DuPont applied more rigorous safeguards to the infrequently entered analyzer house than for the normally occupied manufacturing building.

50. The stairs that provide the primary means to access the Lannate® and API equipment within the manufacturing building are designed for fire escape. However, DuPont has not effectively evaluated entry or exit hazards for the stairways in a toxic or inert gas atmosphere.[70] Furthermore, there is no ventilation provided in the stairway (north or south), and doors between the process and the stairways do not provide an effective barrier to keep the hazardous gases from entering the stairways.

51. The ventilation design is adversely affected by the DuPont operational practice of leaving external doors to the manufacturing building open,[71] resulting in short circuiting of designed air flow patterns. As shown in Figure 24, the ventilation system at times is not even able to remove water vapor from the manufacturing building. The ventilation system performance with higher molecular weight gases such as chlorine and methyl mercaptan would likely be worse as these higher molecular weight gases need more dilution air velocity[72] to sweep them up from the floor and into the exhaust air duct along the ceiling.

[70] Some portions of the manufacturing building can also be accessed by an elevator or with ladders.
[71] Numerous unsealed piping penetrations into and out of the manufacturing building also result in large air gaps (openings) that adversely impact the dilution air flow design.
[72] The higher molecular weight gases are heavier than air and would naturally descend to the ground.

Staff draft that is subject to change, approval, or disapproval by the Board.

Figure 24. Ineffective ventilation on the second floor of the manufacturing building. These photos document an operational activity taking place on January 9, 2015. Operations had directed a hot water hose on a flow meter on the north east side of the second floor as seen in the photo on the left. The photo on the right shows the steam nearly motionless (yellow circle) on the south east side of the building also on the second floor. Although the wet end fan was running at the time, an open door (Figure 25) provided a less restrictive path for air to enter the building and thus very little dilution air ventilation was taking place to sweep potentially hazardous gases out of the south east corner of the room. Note – these photos are snippets from a video recording. The video recording does a much better job of demonstrating the poor ventilation within the yellow circle.

Figure 25. Photo of the open door on the south side of the second floor adversely impacting the dilution air ventilation flow across process equipment described in Figure 24.

Staff draft that is subject to change, approval, or disapproval by the Board.

Neither Workers nor the Public Are Protected by DuPont's Toxic Gas Detection System

52. DuPont's methyl mercaptan technical standard states, "[a]utomatic or continuous specific chemical detection systems *must* be installed where a [methyl mercaptan] release could have any off-site impact […]." The manufacturing building is equipped with gas detectors for methyl mercaptan[73] in various locations. There are two methyl mercaptan detectors on the first floor and one on the fourth floor. All three of the methyl mercaptan detectors inside the manufacturing building are located on the east—wet end side. Despite being required by the technical standard, there were no methyl mercaptan detectors to identify a release on the third floor where the incident took place. Although the methyl mercaptan detectors alarmed at the time of the incident and during the days and hours preceding the incident, these detectors did not provide an effective safeguard to protect workers. The methyl mercaptan concentration in the building[74] was only displayed on the DCS monitor and was not recorded by DuPont.

53. DuPont's methyl mercaptan gas detectors are intended to provide early warning of significant leaks with potential off-site impacts and do not protect workers from exceeding short term exposure limits. The alarm point of the methyl mercaptan detectors (25 ppm) is set at the Emergency Response Planning Guide (ERPG)[75]-2 level—significantly above the OSHA permissible exposure ceiling limit (10 ppm). In addition, OSHA has recognized that its exposure limits for methyl mercaptan are outdated and recommends using the more conservative NIOSH or Cal-OSHA exposure limit (0.5 ppm).[76,77] DuPont's toxic gas monitoring approach allows workers to be exposed to unacceptable hazardous concentrations of methyl mercaptan without an alarm ever going off.

54. Although DuPont's methyl mercaptan technical standard states, "[a]ll DuPont sites *will* protect the site and neighboring businesses and communities from the escape of a highly toxic material[,]" methyl mercaptan detectors provided essentially no value to DuPont personnel or to the public. DuPont operations staff became accustomed to the odor of methyl mercaptan being present in their work environment. The low odor threshold of methyl mercaptan resulted in a

---

[73] DuPont uses a hydrogen sulfide (H_2S) detector to identify methyl mercaptan leaks. DuPont records indicate that the manufacturer has stated the detector should be capable of detecting methyl mercaptan within 1 part per million (ppm).
[74] DuPont's detectors for methyl mercaptan are calibrated for 0-50 parts per million (ppm) using a hydrogen sulfide (H_2S) calibration gas. The alarm for these detectors is set at 25 ppm.
[75] The ERPG is further explained below in paragraph 57. ERPG-2: "The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action." See https://www.aiha.org/get-involved/AIHAGuidelineFoundation/EmergencyResponsePlanningGuidelines/Documents/ERP-SOPs2006.pdf (accessed July 5, 2015).
[76] OSHA recommends that employers consider using the alternative occupational exposure limits because the Agency believes that exposures above some of these alternative occupational exposure limits may be hazardous to workers, even when the exposure levels are in compliance with the relevant PELs. See https://www.osha.gov/dsg/annotated-pels/ (accessed June 15, 2015).
[77] The Cal-OSHA permissible exposure limit (PEL) is an 8-hour time weighted average (TWA) of 0.5 ppm and the NIOSH recommended exposure limit (REL) is a 15-minute ceiling limit of 0.5 ppm. See https://www.osha.gov/dsg/annotated-pels/tablez-1.html (accessed June 15, 2015).

Staff draft that is subject to change, approval, or disapproval by the Board.

false sense of safety. Consequently, the workers did not associate detecting the odor of methyl mercaptan as representing an immediate hazard. Moreover, multiple DuPont employees informed the CSB that odor was the primary method used to locate a methyl mercaptan leak. DuPont personnel routinely responded to methyl mercaptan detector alarms without any additional respiratory protection. When they responded, if a significant leak was identified, these personnel consistently stated they would leave to get an SCBA and then return. On the night of the incident, multiple methyl mercaptan detector alarms activated, but because the workers were aware that methyl mercaptan was being released from their activities associated with clearing the hydrate, these alarms were normalized. No additional personal protective equipment, such as air-purifying respirators or SCBAs was used. In addition, DuPont did not order a unit evacuation and did not notify the ERT until hours later, after the operator made the distress call.

55. DuPont highly toxic material standards require that toxic gas detection systems be treated the same as safety interlocks.[78] A January 2014 DuPont audit finding identified that appropriate safety actions were not taking place when highly toxic chemical gas detectors alarmed. The audit report stated, "[h]owever, during the last two events with high levels on area chlorine detectors no area or plant alarms were sounded, the ERT was not notified, and the area was not cleared of personnel."[79] Although the audit finding was closed in June 2014, the retraining sessions DuPont conducted were not sufficient to address the concern identified. As stated above, hours prior to the November 15, 2014 incident, multiple highly toxic chemical gas detectors alarmed (sounded). In addition, highly toxic methyl mercaptan releases on November 13 and 14, 2014, resulted in methyl mercaptan detector alarms, but these events were never reported as releases nor investigated as serious process safety incidents. Consequently, these gas detector systems were not treated the same as safety interlocks.

Relief System Design Endangers Workers and the Public

56. DuPont has been in the process of implementing a five-year program at La Porte to ensure pressure relief systems conform with existing DuPont standards, process safety regulations, and industry codes and standards. DuPont has not made this program a sufficiently high priority, has limited internal resources, and has fallen far behind schedule. The program was initiated in 2011 with a 2015 completion goal. Although the program is more than four years into the five-year plan, IBU relief systems are only 35% complete. In addition, after conducting numerous employee interviews and reviewing many DuPont documents such as PHAs and relief system designs, the CSB has concluded that DuPont has not effectively evaluated relief valve scenarios and discharge location safety to ensure the community, workers, and the environment are protected from these process safety hazards.

[78] DuPont defines a safety interlock as a system or function that detects an out-of-limits (abnormal) condition or improper sequence and brings it to a safe condition.
[79] ERT is an acronym for the Emergency Response Team.

Staff draft that is subject to change, approval, or disapproval by the Board.

Methyl Mercaptan Storage Tank Relief System

57. In 2002, DuPont evaluated the potential to exceed off-site concentrations from a release of methyl mercaptan through the relief valves on top of the 18,000 gallon methyl mercaptan storage tank shown in Figure 26. The American Industrial Hygiene Association (AIHA) publishes Emergency Response Planning Guide (ERPG) concentration values for single exposure to chemicals.[80] ERPG values are a health-based guideline to aid in emergency planning. The three levels of ERPG are published in increasing level of consequence: ERPG-1; ERPG-2; and, ERPG-3.[81] ERPG-3 is considered a worst-case planning level above which there is the possibility that some members of the community may develop life threatening health effects.[82] The off-site concentrations that DuPont evaluated in 2002 were ERPG-3.

58. In its 2002 management of change document, DuPont described the existing situation as, "[t]he S23A Corporate Standard for Highly Toxic Materials requires mitigation of offsite MeSH [methyl mercaptan] release from fire." DuPont's evaluation found that in the event of a fire these relief valves could release 10,000 pounds per hour of methyl mercaptan and result in an off-site concentration that would exceed the ERPG-3 value of 100 ppm.[83] To mitigate this risk to neighboring communities, DuPont invested over $17,000 to insulate the tank. A properly insulated tank can increase the time for a fire to heat the tank contents by reducing the heat input and causing less gas to be released from the relief system. DuPont documented the purpose and technical basis of this change stating, "[i]nsulating the tank would reduce offsite impact of RV [relief valve] discharge to acceptable concentration limits without need for more expensive mitigation options. We need to keep the relief rate below 4500 lb/hr [pounds per hour] to avoid ERPG-3 concentrations." DuPont's corporate standard for highly toxic materials states:

> *Under all circumstances, potential discharges from pressure-relieving devices (e.g., those associated with transportation equipment used as long-term storage or connected storage or feed tanks) must be within acceptable concentration limits and of sufficiently short duration so that people off-site are not exposed to a dose that could result in either life-threatening (i.e., ERPG-3) or irreversible (i.e., ERPG-2) health effects.*

---

[80] See https://www.aiha.org/get-involved/AIHAGuidelineFoundation/EmergencyResponsePlanningGuidelines/Documents/ERP-SOPs2006.pdf (accessed March 24, 2015).

[81] The ERPG values for methyl mercaptan in parts per million (ppm) are: ERPG-1, 0.005; ERPG-2, 25; ERPG-3, 100. See https://www.aiha.org/get-involved/AIHAGuidelineFoundation/EmergencyResponsePlanningGuidelines/Documents/2014%20ERPG%20Values.pdf (accessed March 24, 2015).

[82] "The values derived for ERPGs should not be expected to protect everyone but should be applicable to most individuals in the general population. In all populations there are hypersensitive individuals who will show adverse responses at exposure concentration below levels where most individuals normally would respond. Furthermore, since these values have been derived as planning and emergency response guidelines, not exposure guidelines, they do not contain the safety factors sometimes incorporated into exposure guidelines. Instead, they are estimates, by the committee, of the thresholds above which there would be an unacceptable likelihood of observing the defined effects." Ibid at p 21.

[83] "Once the distance from the release to the ERPG-3 level is known, the steps to mitigate the potential for such a release can be established." Ibid at p 1.

Staff draft that is subject to change, approval, or disapproval by the Board.

59. In addition, the American Petroleum Institute (API) publishes an industry standard on Pressure-relieving and Depressuring Systems, API Standard 521 (API 521). When evaluating the atmospheric release of toxic chemicals from a relief device, API 521 states, "[c]oncentrations of toxic vapors, at the company property line, shall not exceed levels that cause life threatening health effects (e.g. ERPG-3 or equivalent)."[84,85]

60. The American Society of Mechanical Engineers' (ASME) Boiler and Pressure Vessel Code also requires that relief valve discharge piping be routed "[…]to a safe place of discharge."[86]

61. However, the insulation on DuPont's methyl mercaptan storage tank intended to limit the relief rate and to protect the community from potential ERPG-3 concentrations was subsequently removed (Figure 26). DuPont lacks management of change or other documentation to indicate technical reasons or management approval for the removal of the insulation. In addition, the "more expensive mitigation options" referenced during the decision to insulate the tank, such as chemical treatment with a caustic scrubber, were not implemented.[87] The CSB has been unable to determine when the insulation was removed, because DuPont lacks documentation and current DuPont personnel were unaware of the tank ever being insulated to mitigate toxic gas exposure to the public. Without the insulation on the methyl mercaptan storage tank, DuPont calculations indicate that the flow rate from the relief valve to atmosphere is approximately 10,000 pounds per hour—more than double the quantity DuPont determined could result in life threatening (ERPG-3) concentrations within the neighboring community. As a result, workers and the public have been exposed to unacceptable risks. After the CSB identified this issue and communicated it to DuPont management, DuPont informed the CSB that the methyl mercaptan storage tank would be reinsulated.

62. Although DuPont's analysis indicates that insulation on the methyl mercaptan storage tank can prevent highly toxic off-site ERPG-3 concentrations, DuPont's internal corporate requirement is to prevent ERPG-2 concentrations. The CSB recommends (2015-01-I-TX-R1) that DuPont evaluate inherently safer design (ISD) options and effectively apply the hierarchy of controls such that neither workers nor the public is harmed from highly toxic chemical releases.

---

[84] API Standard 521, Pressure-relieving and Depressuring Systems, Sixth Edition, January 2014.
[85] This safety provision applies to users who apply a consequence-based approach. The API Standard 521 also allows a risk-based approach to establish appropriate acceptance criteria.
[86] American Society of Mechanical Engineers (ASME), 2013. "Rules for Construction of Pressure Vessels," ASME Boiler and Pressure Vessel Code, Section VIII, Division 1. UG-135 (f); pg. 100.
[87] A 2005 document indicates that the insulation installed on the methyl mercaptan storage tank in 2002 resulted in corrosion to the methyl mercaptan storage tank and further implied that the insulation would be repaired. There was no indication that simply removing the insulation was an option.

Staff draft that is subject to change, approval, or disapproval by the Board.

Figure 26. Methyl mercaptan storage tank showing atmospheric relief valves (yellow circle). At present, the storage tank is not insulated and there does not appear to be any mitigation to prevent off-site ERPG-3 concentrations as required by American Petroleum Institute and DuPont standards.

Staff draft that is subject to change, approval, or disapproval by the Board.

Nitrogen Pressure Control Relief System

63. Another example of relief valve discharge not currently being routed to a safe location is shown in Figure 27. These nitrogen relief valves discharge directly under a pipe rack in close proximity to worker entry/exit points to the manufacturing building. Should these relief valves open, it is unlikely that the nitrogen would be sufficiently dispersed. Consequently, nitrogen discharge from these relief valves may result in an asphyxiation hazard to workers. DuPont engineering standards prohibit this design. For pressure relief discharge piping the engineering standard states:

> *When discharging directly to the atmosphere, discharge shall not impinge on other piping or equipment and shall be directed away from platforms and other areas used by personnel.*

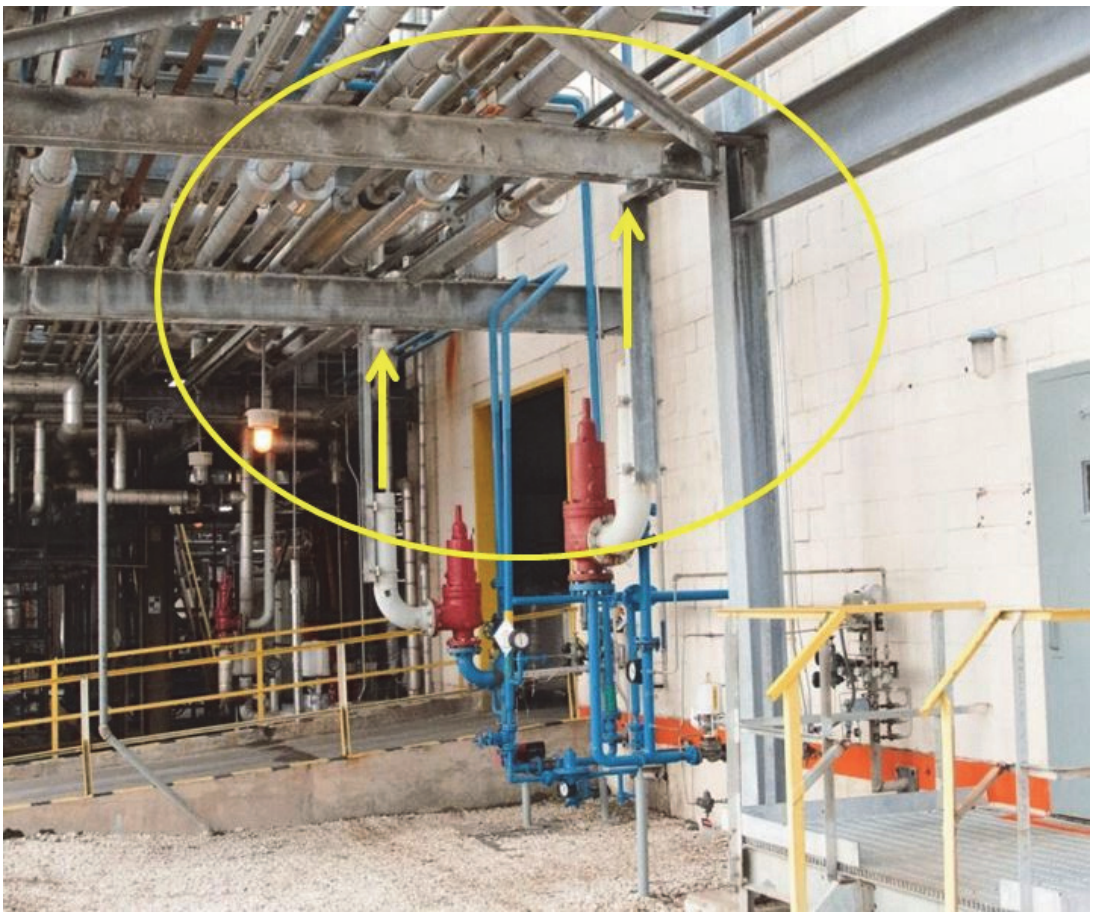

Figure 27. Nitrogen relief valves near south entrance of the manufacturing building. Dispersion from these atmospheric nitrogen relief valves is obstructed by an overhead pipe rack. This obstruction could result in a dangerous atmosphere to workers as they enter or exit from the manufacturing building.

Staff draft that is subject to change, approval, or disapproval by the Board.

Caustic Scrubber Relief System

64. On December 16, 2014, highly toxic chlorine was released from a caustic scrubber relief valve (Figure 28 left photo) during an operation to vent and disconnect a chlorine railcar from the process. DuPont documentation indicates that the relief valve discharge piping is 10 feet above the work platform. This 10-foot value is used to help ensure relief valves discharge to a safe location.[88] However, an evaluation of the relief valve in the field indicates that while this 10-foot vertical safety margin exists for the immediate work platform, there are several other adjacent work platforms above the relief valve discharge piping as shown in Figure 28 (right photo). As a result, these adjacent work platforms are not safe locations for workers because highly toxic gas could be discharged towards them. The design of the relief valve discharge location should be thoroughly evaluated for safety.

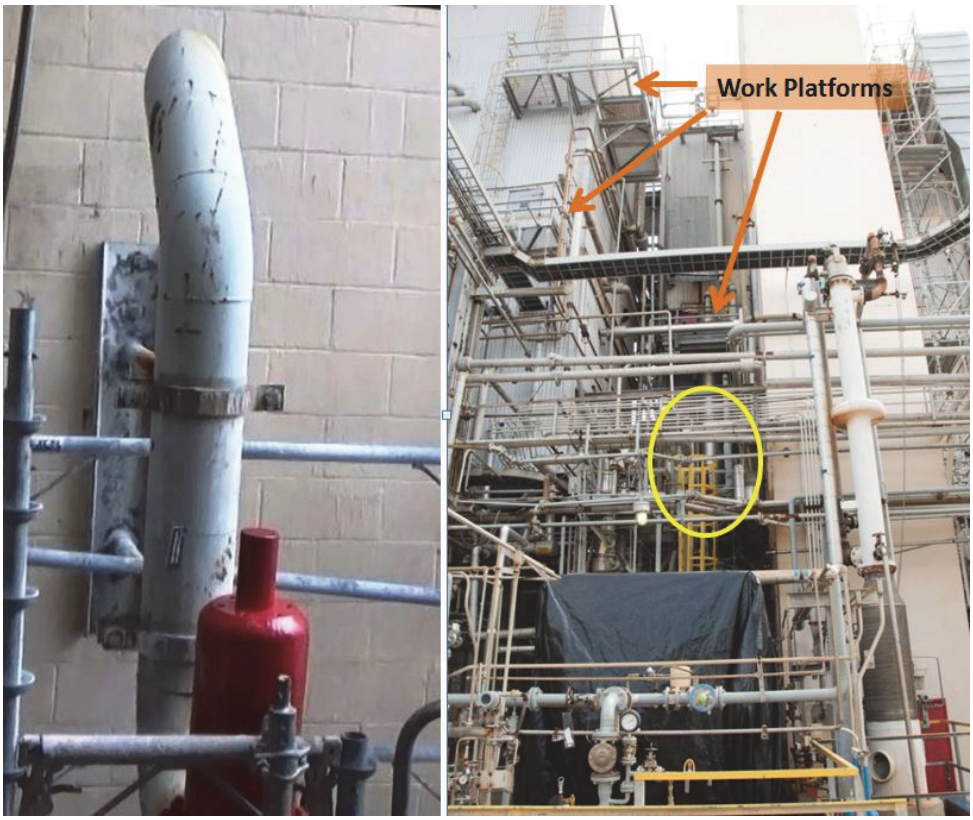

Figure 28. Caustic scrubber pressure relief device location. The photo on the left shows the relief valve within the yellow circle in the photo on the right. This caustic scrubber relief valve is located in a congested area on the north side of the manufacturing building. Although DuPont documentation indicates the discharge piping of this relief valve is 10 feet above the work platform, the analysis failed to consider the other work platforms above this relief valve that can clearly be seen (orange arrows) in the photo on the right. On December 16, 2014, this relief valve was the source of a highly toxic chlorine release when a DuPont operations activity vented chlorine to the caustic scrubber in order to disconnect and relocate a chlorine railcar.

[88] The discharge from safety-relief valves shall be piped vertically upward to a point at least 10 feet above the ground. The discharge lines or pipes shall be adequately supported and protected against physical damage. See 29 CFR §1910.110(h)(4)(iii)(a)(2007).

Staff draft that is subject to change, approval, or disapproval by the Board.

Methyl Mercaptan Piping Relief System

65. The methyl mercaptan pump that feeds the Lannate® process is equipped with relief valves designed such that they could discharge highly toxic, highly flammable liquid directly to the ground in the immediate vicinity of where an operator would be located when starting the pump (Figure 29). In the 1990s, DuPont eliminated a similar set of relief valves for the API process pump. Despite it being immediately adjacent and similarly designed, the Lannate® methyl mercaptan pump's relief valves remained. Furthermore, no PHA or engineering analysis has evaluated the Lannate® methyl mercaptan pump's relief valve discharge location to ensure worker safety.

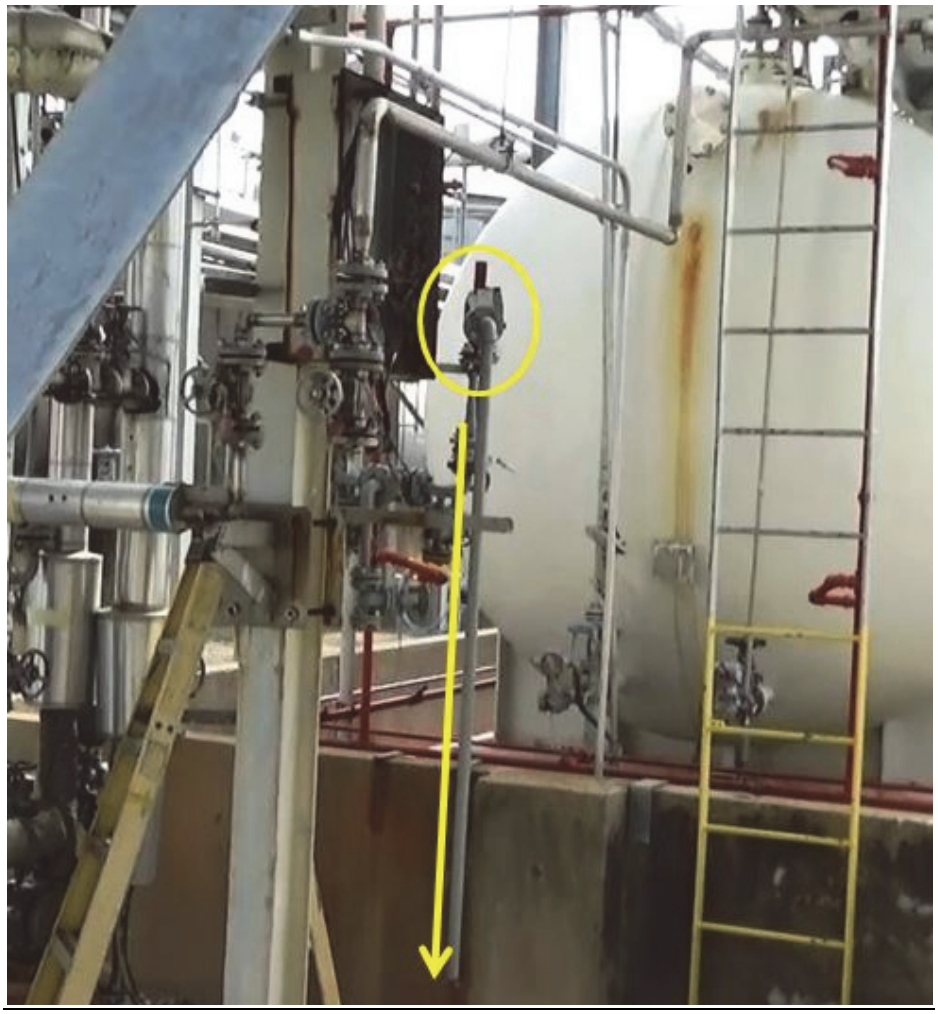

Figure 29. Liquid methyl mercaptan relief valve on the discharge of the methyl mercaptan pumps is designed to discharge this highly toxic, highly flammable chemical to grade just north of the methyl mercaptan storage tank.

Staff draft that is subject to change, approval, or disapproval by the Board.

Nitrogen to Methyl Mercaptan Railcar Unloading Relief System

66. The design of the nitrogen relief valves at the railcar loading and unloading stations (Figure 30) did not consider a scenario where the relief valves could be lined up to the discharge of the methyl mercaptan pumps, as they were at the time of the incident. The methyl mercaptan pump discharge pressure (90 psig)[89] is higher than the set pressure (80 psig) of these nitrogen relief valves. Therefore, the methyl mercaptan pump will cause the relief valve to open and release the highly toxic and highly flammable chemical to the atmosphere. When tested post-incident, three of the four nitrogen rupture discs were ruptured and all four of the nitrogen relief valves leaked.[90] Because the rupture discs and relief valves would not hold pressure when tested, an atmospheric release of highly toxic and highly flammable liquid methyl mercaptan likely occurred during the incident through this relief system that was intended to release and disburse nitrogen vapor. This relief system is part of the 35% of systems that DuPont considers complete and in compliance with industry codes and standards. However, the alignment of block valves at the time of the incident revealed a highly toxic methyl mercaptan release scenario that DuPont's five-year relief system program never considered. Consequently, this program has not been fully effective.

Figure 30. This photograph shows the nitrogen relief valves at one of the two methyl mercaptan railcar unloading stations. The nitrogen relief systems for each of the two railcar unloading stations are nearly identical. DuPont PHAs and relief valve design documents never considered the possibility of the methyl mercaptan storage tank pumps being lined up to these relief valves – as it was at the time of the incident. As a result, liquid methyl mercaptan was discharged from a system designed for nitrogen vapor.

[89] psig is an acronym for pounds per square inch gauge (pressure).
[90] The relief valve repair shop was unable to achieve a successful "pop" test on these valves because the leak rate through the valve was too great to build up sufficient pressure to fully open the relief valve.

Staff draft that is subject to change, approval, or disapproval by the Board.

Process Hazard Analyses

67. The manufacturing building ventilation system has never been evaluated by a process hazard analysis (PHA). Prior to the incident, DuPont identified this shortcoming. However, DuPont's pre-incident PHA schedule indicates that the initial PHA of the manufacturing building ventilation system would not occur until 2017. This ventilation system includes the "PSM Critical" fans that were not working at the time of the incident.

68. Following the November 15, 2014 incident, DuPont completed two new baseline PHAs using a more robust PHA methodology for the IBU.[91] Despite performing PHAs for more than 30 years, DuPont employees told CSB investigators that the improved approach for conducting PHAs was resulting in hundreds of action items, never previously identified to control hazards. There are 13 additional PHAs to cover the full Insecticides Business Unit. DuPont has agreed to develop and implement a revised schedule to expedite the cyclical reviews for the remaining IBU PHAs. The final schedule will prioritize high-hazard processes. Some of these PHAs will be redone prior to restart. In addition, DuPont has retained a third-party consultant to review the existing IBU PHAs prior to restart.

[91] The more robust PHA methodology applied was a Structured "What If" technique developed internally by DuPont. "The methodology incorporates the underlying principles of Hazard and Operability Analysis (HAZOP), failure mode and effect analysis (FMEA) "What if" and Checklist, but in a more user-friendly manner, with the intention to produce a result of equivalent or superior quality than any of these other methods applied alone."

Staff draft that is subject to change, approval, or disapproval by the Board.

CSB Investigation Reports are formal, detailed reports on significant chemical accidents and include key findings, root causes, and safety recommendations. CSB Hazard Investigations are broader studies of significant chemical hazards. CSB Safety Bulletins are short, general-interest publications that provide new or noteworthy information on preventing chemical accidents. CSB Case Studies are short reports on specific accidents and include a discussion of relevant prevention practices. All reports may contain include safety recommendations when appropriate. CSB Investigation Digests are plain-language summaries of Investigation Reports.

The U.S. Chemical Safety and Hazard Investigation Board (CSB) is an independent Federal agency whose mission is to ensure the safety of workers, the public, and the environment by investigating and preventing chemical incidents. The CSB is a scientific investigative organization; it is not an enforcement or regulatory body. Established by the Clean Air Act Amendments of 1990, the CSB is responsible for determining the root and contributing causes of accidents, issuing safety recommendations, studying chemical safety issues, and evaluating the effectiveness of other government agencies involved in chemical safety.

No part of the conclusions, findings, or recommendations of the CSB relating to any chemical accident may be admitted as evidence or used in any action or suit for damages. See 42 U.S.C. § 7412(r)(6)(G). The CSB makes public its actions and decisions through investigation reports, summary reports, safety bulletins, safety recommendations, case studies, incident digests, special technical publications, and statistical reviews. More information about the CSB is available at www.csb.gov.

CSB publications can be downloaded at www.csb.gov or obtained by contacting:
U.S. Chemical Safety and Hazard Investigation Board
Office of Congressional, Public, and Board Affairs
1750 Pennsylvania Ave NW, Suite 910
Washington, DC 20006
(202) 261-7600

Staff draft that is subject to change, approval, or disapproval by the Board.