

Risk of Chemical Accidents During Process Startup

This purpose of this Enforcement Alert is to highlight the importance of accident prevention efforts during startup periods and other times of nonroutine operations. Chemical accidents can occur at any time, but there are times when facilities are more prone to accidents. Startup is a particularly vulnerable time. The Chemical Safety Board (CSB) noted in its Safety Digest, “CSB Investigations of Incidents During Startups and Shutdowns” (https://www.csb.gov/assets/1/6/csb_digest_-_startup_shutdown.pdf) and in its Safety Alert, “AFTER HARVEY: Precautions Needed During Oil and Chemical Facility Startup” (https://www.csb.gov/assets/1/20/csb_harvey2017_05.pdf), that a disproportionate number of accidents occur during startup or other nonroutine operations. Facilities should be aware of several recent incidents (described below) that occurred during startup, so they can take extra care to avoid these types of accidents.

Legal Requirements

Preventing chemical accidents is an important responsibility for facilities that use extremely hazardous substances. Section 112(r)(7) of the Clean Air Act and the implementing regulations at 40 CFR Part 68 require all facilities, regardless of their size, that use certain extremely hazardous substances above a specified quantity in a process to develop a Risk Management Program. These facilities must:

- Conduct a hazard assessment that identifies potential effects of a chemical accident and an evaluation of worst-case and alternative accidental release scenarios (40 CFR Subpart B);
- Keep track of any accidents that took place in the last five years (40 CFR 68.42);
- Implement a prevention program that includes safety precautions, and maintenance, monitoring, and employee training measures (Subpart C, and Subpart D); and
- Implement an emergency response program that includes coordination with local emergency responders, procedures for responding to accidental releases, emergency health care, employee training measures and procedures for informing the public and response agencies (e.g., fire departments) should an accident occur (40 CFR Subpart E).

Subpart G of 40 CFR Part 68 also requires these facilities to submit a written Risk Management Plan that summarizes their Risk Management Program to the U.S. Environmental Protection Agency (EPA). The information in a facility’s Risk Management Plan helps local fire, police, emergency response personnel, and other stakeholders prepare for and respond to chemical accidents. It also provides citizens with useful information about chemical hazards in their communities.

National Compliance Initiative

While EPA routinely monitors compliance with accident prevention requirements and takes appropriate action if companies are not meeting their legal obligations to operate in a safe manner, these requirements are also currently the subject of a National Compliance Initiative (NCI). Through the NCI, EPA is increasing its compliance and enforcement activities to ensure companies are reducing the likelihood of chemical accidents and improving the response to accidents that do occur. More information about the NCI can be found at <https://www.epa.gov/enforcement/national-compliance-initiative-reducing-accidental-releases-industrial-and-chemical>.

Serious Chemical Incidents Occurring During Startup

In the immediate aftermath of an accident, local fire, police and emergency responders are generally first on the scene to respond to the fire or chemical release. That is why it is important for them to have a facility's Risk Management Plan so that they are better prepared to respond to the hazards they might be facing. The Chemical Safety Board investigates accidents to determine the cause or causes so that similar accidents might be prevented. The EPA would also investigate after an accident to determine if the facility was in violation of Section 112(r) that might have led to the incident. If it was in violation, the EPA will compel the company to return to compliance and may assess a penalty. The following are examples of serious chemical incidents.

Fire during Startup at Phillips 66 Wood River Refinery Caused Injury

On February 10, 2019, a fire occurred in the Distilling Unit #2 at the Phillips 66 Wood River Refinery during startup after a planned maintenance outage. Hydrocarbons were routed to a heat exchanger, which should have been bypassed, when operators opened the incorrect valve. The liquids flowed into the exchanger shell side and over-pressured a bellows on the tube side, releasing hydrocarbons through an open pipe. The hydrocarbons sprayed out of the open pipe onto the exchanger platform structure and found an ignition source. Approximately 50,000 pounds of the hydrocarbon flammable mixture were released over eight minutes and the subsequent fire lasted about 50 minutes. One contractor employee was injured in the incident.

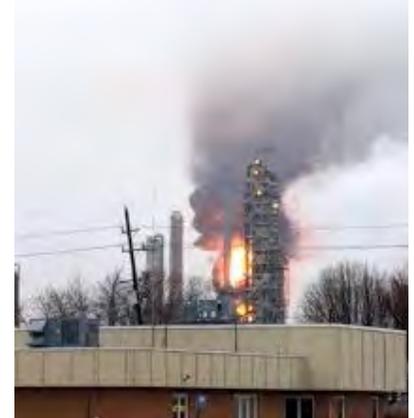


Figure 1: Fire at Phillips 66 Wood River Refinery

Fire during Preparations for Startup at Kuraray America Caused Numerous Injuries

On May 19, 2018, at approximately 10:30 a.m., a fire occurred at the Kuraray America EVAL facility in Pasadena, Texas during preparations for startup activities following a turnaround. At the time of the incident, 266 employees and contract workers were onsite. During pre-startup pressure-testing activities of a chemical reactor, an abnormal high-pressure condition developed and over 2,000 pounds of ethylene were released to the atmosphere from a pressure relief valve. The ethylene vapors ignited causing worker injuries. Twenty-one injured workers were transported to off-site medical facilities for treatment.

The CSB investigation into the underlying causes of this incident is ongoing as of the date of this alert. More information can be found at: <https://www.csb.gov/kuraray-america/>.

Release during Startup at DuPont La Porte Chemical Facility

On November 15, 2014, Dupont La Porte released 24,000 pounds of methyl mercaptan from vent piping at an insecticide production plant in La Porte, Texas during startup and troubleshooting operations. The release killed four employees and injured an additional two employees.



Figure 2: DuPont La Porte Chemical Facility

The DuPont Lannate® process had undergone a shutdown on November 10 and a portion of the methyl mercaptan piping in the reaction section of the process became plugged due to formation of a solid hydrate. Plant personnel conducted troubleshooting for several days in this section of the plant and ultimately identified the location of the plug and dislodged it by using hot water on the outside of the piping. Plant personnel opened valves from the mercaptan piping to the waste gas vent header to relieve pressure in the system. The

vent header provided an open path to the interior of a building through drain lines that would later be opened in the troubleshooting process. When the solid hydrate began to dissolve, methyl mercaptan liquids entered the vent header and released into the building. Multiple plant personnel who were troubleshooting the plugged lines and responding to alarms within the building became incapacitated, eventually leading to injuries and death.

The CSB investigated the incident and identified multiple deficiencies in the process safety management and emergency response programs at the plant that contributed to the accident during the Lannate process start-up. The facility's inadequate emergency response procedures and failure to maintain emergency response equipment led to delays in the plant Emergency Response Team's ability to enter the building and respond to the incident. The facility's 2011 process hazards analysis (PHA) identified the formation of methyl mercaptan hydrate solids as a hazard but did not include any recommendations to address the hazard that may have prevented the accident. The facility applied hot water to the methyl mercaptan piping and opened several valves to the vent header without conducting a management of change (MOC) review that may have identified the hazards. In addition, operators opened drain lines along the vent header while troubleshooting without following safe work practices for line openings. The CSB report can be found at <https://www.csb.gov/dupont-la-porte-facility-toxic-chemical-release/>.

EPA and the Department of Justice recently concluded an enforcement action against DuPont for alleged violations that led to a fatal release. As a result of that enforcement action, DuPont paid a \$3.1 million penalty. More information about this action can be found at <https://archive.epa.gov/epa/newsreleases/epa-and-justice-department-reach-31-million-settlement-dupont-alleged-chemical-accident.html>.

Release during Startup at Williams Geismar Olefins Plant Results in Fatalities

On June 13, 2013, a reboiler on the propylene fractionator distillation column at the Williams Geismar Olefins plant ruptured during start-up operations, releasing over 30,000 pounds of hydrocarbons that ignited and caused an explosion and fire. The accident killed one operator on-site and a supervisor the following day, injured 167 additional employees and contractors, and forced a shelter-in-place for the surrounding community in a two-mile radius. A reboiler is a shell-and-tube heat exchanger that exchanges heat between quench water on the tube-side and the recycled propylene process stream on the shell side, which vaporizes the



Figure 3 Reboiler, post-accident

hydrocarbons before returning them to the distillation column. The Geismar plant alternated between two exchangers, Reboiler A and Reboiler B, with one exchanger on-line and one exchanger valved out as a spare for use if needed. Prior to the accident, operators observed a reduced flowrate of the quench water feeding the on-line exchanger, Reboiler A, and suspected fouling of the water. To take Reboiler A out of service, operators switched valves to begin flow of quench water to Reboiler B while keeping the shell-side valves closed. Soon after, Reboiler B over-pressured and ruptured. The ensuing investigation determined that hydrocarbons had either leaked into or were inadvertently fed to Reboiler B at some point prior to the accident and the trapped liquids vaporized and over-pressured the system causing an explosion.

The CSB investigated the incident and discovered multiple deficiencies in the process safety management program at the plant contributed to the accident during start-up. Inadequate MOC procedures and implementation of those procedures failed to identify the over-pressurization hazards of trapped hydrocarbons in the exchangers introduced by installation of the isolation block valves in years prior to the incident. Operating procedures in place at the start-up of the Reboilers were generic and did not identify the specific valves, equipment, and sequencing of steps needed to safely start up the offline exchanger. The questions on the pre-startup safety review (PSSR) checklist completed at the time of the valve installation were incomplete or incorrectly answered. If correctly answered, the hazards may have been identified. PHAs performed on this process either did not identify the over-pressurization hazard or safeguards to protect from over-pressurization were not completed. The CSB report can be found at <https://www.csb.gov/williams-olefins-plant-explosion-and-fire/>.

The EPA and the Department of Justice settled a civil enforcement action against Williams Olefins for alleged violations that resulted in a fatal accident. Williams paid a penalty of \$750,000.

Audit Policy

Regulated entities of any size who voluntarily discover, promptly disclose, expeditiously correct, and take steps to prevent recurrence of potential violations may be eligible for a reduction or elimination of any civil penalties that otherwise might apply. Most violations can be disclosed and processed via EPA's automated online "eDisclosure" system

(<https://www.epa.gov/compliance/epas-edisclosure>). To learn more about the EPA's violation disclosure policies, including conditions for eligibility, please review EPA's Audit Policy website at <https://www.epa.gov/compliance/epas-audit-policy>. Many states also offer incentives for self-policing; please check with the appropriate state agency for more information.

Where can I get more information?

For more information, please visit EPA's Risk Management Plan (RMP) Rule webpage at <https://www.epa.gov/rmp>

Facilities that use listed extremely hazardous substances need to comply with these Important Regulatory Provisions

Facilities that use listed extremely hazardous substances need to comply with all the regulatory provisions of 40 CFR Part 68, to the extent they are applicable. In order to prevent accidents during startup, the following provisions are particularly important:

- Operating Procedures (40 CFR 68.52 and 68.69), that provide clear instructions for safely conducting activities involved in each covered process.
- Training (40 CFR 68.54 and 68.71), so that each employee involved in operating a process is familiar with the operating procedures, safety and health hazards, emergency operations, and safe work practices.
- Pre-startup review (40 CFR 68.77), ensuring that construction and equipment is in accordance with design specifications, and that safety, operating, maintenance, and emergency procedures are in place and are adequate.

Disclaimer

This Enforcement Alert addresses select provisions of EPA regulatory requirements using plain language. Nothing in this Enforcement Alert is meant to replace or revise any Clean Air Act permit, any EPA regulatory provision, or any other part of the Code of Federal Regulations, the Federal Register, or the Clean Air Act.