

CASE STUDY



Uncontrolled Oleum Release Petrolia, Pennsylvania (Three towns evacuated)

2009-01-I-PA
September 2009



This case study examines an oleum release that occurred on the afternoon of Saturday, October 11, 2008, in Petrolia, Pennsylvania. During a transfer operation, an oleum (fuming sulfuric acid) process tank overflowed, filled an exhaust ventilation system, and released the oleum into a storage building. The oleum release created a cloud of sulfuric acid mist that filled the building. The sulfuric acid cloud flowed out to the facility grounds and beyond the fence line into the surrounding community. Plant personnel evacuated the facility and community emergency responders ordered the evacuation or shelter-in-place of about 2,500 residents from the towns of Petrolia, Bruin, and Fairview.

Key Issues:

- Temporary Change Evaluation
- Safeguard Evaluation
- Process Hazard Analysis

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1.0 Introduction

Just after 3:00 pm on Saturday, October 11, 2008, a tank located in a storage building at the INDSPEC Chemical Corporation (INDSPEC) resorcinol facility in Petrolia, Pennsylvania, overflowed during an oleum transfer. Oleum, a mixture of sulfuric acid and sulfur trioxide, filled the exhaust ventilation system (vent system)¹ connected to the tank and eventually released into the storage building. The release of oleum created a cloud of sulfuric acid mist that filled the building and flowed out of the facility into the community.

As the oleum storage tank overflowed, the storage building filled with a dense mist, and liquid oleum spilled from the vent system. Faced with an uncontrolled release, the INDSPEC incident commander declared a plant-wide emergency, notified local fire departments, and requested mutual aid services. Facility personnel evacuated.

While INDSPEC emergency responders managed the onsite incident, at 5:14 pm community emergency responders ordered the evacuation or shelter-in-place² of about 2,500 nearby residents from the towns of Petrolia, Bruin, and Fairview.³ The evacuation order continued until about 2:00 am.

1.1 INDSPEC Chemical Corporation

Koppers Company, Inc. owned and operated the Petrolia facility until 1988. In late 1988, after the Beazer organization⁴ acquired Koppers Company, Inc., the Petrolia facility and a nearby research center formed INDSPEC in a management buyout. In 1996, Occidental Petroleum Corporation acquired an interest in INDSPEC. Finally, in 1999, the Occidental Petroleum Corporation acquired all remaining INDSPEC stock. INDSPEC is an indirect, wholly owned subsidiary of Occidental Petroleum Corporation.

The facility produces resorcinol, a chemical used in the rubber industry as an automobile tire adhesive.

¹ The exhaust ventilation system comprises ducts connected to each of the oleum tanks and an air pollution control device to remove sulfuric acid and sulfur trioxide.

² Shelter-in-place can protect people in emergencies by reducing their exposure to toxic substances. People should take refuge in a small interior room, close windows, seal openings, and shut off heating and air conditioning systems.

³ The evacuation zone included populated areas north, south, and west of the facility.

⁴ Beazer is a British construction and building materials firm.

Resorcinol is also used as a chemical intermediate in the manufacture of pharmaceuticals and other organic chemicals. Oleum is a raw material used in resorcinol production.

1.2 The Petrolia Facility

The facility is located in Petrolia, Pennsylvania, a borough of about 200 people roughly 40 miles northeast of Pittsburgh. Residences and commercial buildings surround much of the facility, which is at the base of an industrialized valley (Figure 1).⁵



Aerial photo courtesy Pennsylvania Spatial Data Access, The Pennsylvania State University

Figure 1. Aerial view of Petrolia Valley

The resorcinol process (the process) normally operates 24 hours a day, seven days a week. Operators work in the oleum storage building on weekdays between about 7:00 am and 3:00 pm and on weekends as necessary.

The oleum storage building, containing three horizontal pressure vessels and two vertical process tanks (Figure 2), is located near the center of the facility. Operators use air pressure to transfer oleum from railcars into the pressure vessels, each of which can hold the contents of two full railcars. Operators

⁵ Two other large chemical facilities occupy the valley in Petrolia and Karns City.

then pump oleum from the pressure vessels to either of the process tanks. While the manufacturing process operates, oleum flows continuously from the process tanks to the resorcinol production unit.

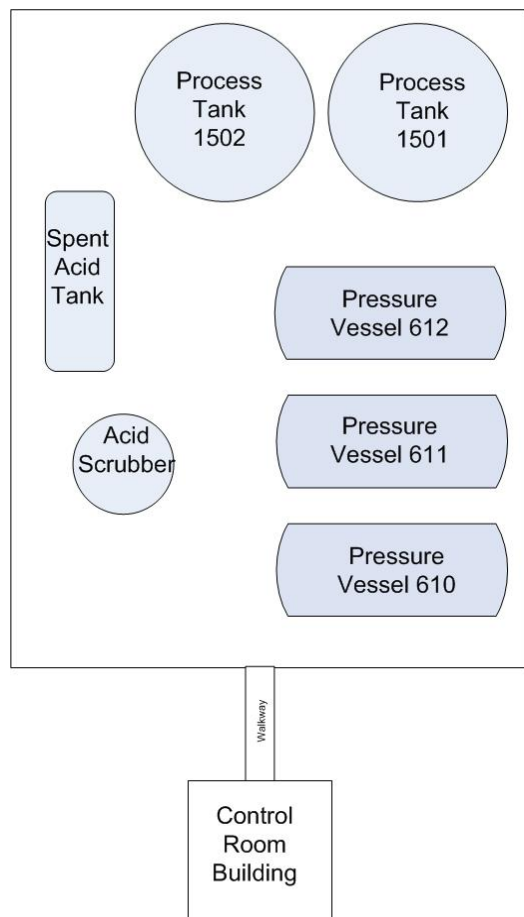


Figure 2. Oleum storage and control room buildings

1.3 Oleum

Oleum, also known as fuming sulfuric acid, is a mixture of sulfuric acid (H_2SO_4) and sulfur trioxide (SO_3). Oleum, when released or spilled, gives off sulfur trioxide gas. The gas reacts with moisture in air and forms a cloud of sulfuric acid mist composed of easily inhaled droplets, some less than 1 micrometer in diameter. A sulfuric acid cloud is dense, visible, and slow moving. Inhaling sulfuric acid droplets can irritate the respiratory system, causing airway constriction and spasms.⁶ Severe exposure can result in fluid in the lungs, internal bleeding, and even death.

The Occupational Safety and Health Administration (OSHA), in 29 CFR 1910.1000, and National Institute for Occupational Safety and Health have set an eight-hour exposure limit for sulfuric acid, and the American Industrial Hygiene Association has set a one-hour maximum exposure limit.⁷ The U.S. Environmental Protection Agency (EPA) requires planning for potential oleum releases under its Chemical Accident Prevention regulations for facilities that store or process greater than 10,000 pounds.⁸

⁶ A detectable odor and irritation due to exposure generally occur at sulfuric acid concentrations above 1 mg/m^3 .

⁷ The eight-hour exposure limit for sulfuric acid is 1 mg/m^3 . The one-hour exposure limit without life-threatening health effects for sulfuric acid is 30 mg/m^3 .

⁸ The EPA set 0.01 mg/L (1 mg/m^3) as the defined toxic endpoint for planning purposes under 40 CFR 68.

2.0 Oleum Storage Building Operations

Three INDSPEC operators perform bulk liquid loading and unloading jobs, one in the oleum storage building and two throughout the rest of the facility. The three operators work Monday through Friday on day shift and rotate among the three jobs weekly.

The oleum storage building operator unloads oleum, benzene, and soda ash from railcars and prepares a soda ash solution. He also pumps oleum from the pressure vessels to the process tanks (Figure 2) and monitors the oleum storage system from the distributed control system (DCS).⁹ The operator's DCS console is in a separate building (control room) adjacent to the oleum storage building.

The oleum storage-building operator is often required to perform work on weekends, which may include mixing soda ash solution or unloading benzene. The facility may schedule this work prior to the weekend or call an operator to the plant as necessary. Operators transfer oleum to the process tanks as part of their weekend duties to ensure that the pressure vessels are empty or nearly empty on Monday mornings.

2.1 Transferring Oleum

Operators transfer oleum from railcars to the pressure vessels and then to the process tanks. To transfer from a railcar, an operator connects a transfer hose to the railcar and pressurizes the railcar with plant air, forcing oleum to the selected pressure vessel.

To pump oleum from a pressure vessel to a process tank, an operator plugs a pump power cord into a power supply (Figure 3). Each of the three pressure vessels has a dedicated transfer pump with a power cord and plug. While there are three power cords and plugs, there is only one (normal) power supply receptacle. The operator plugs the power cord into the normal receptacle in the oleum storage building and starts the pump using the DCS console in the adjacent control room. When transfer is complete, the operator stops the pump on the DCS console and returns to the oleum storage building to unplug the power cord.

Figure 4 shows the power supply arrangement on the day of the incident.

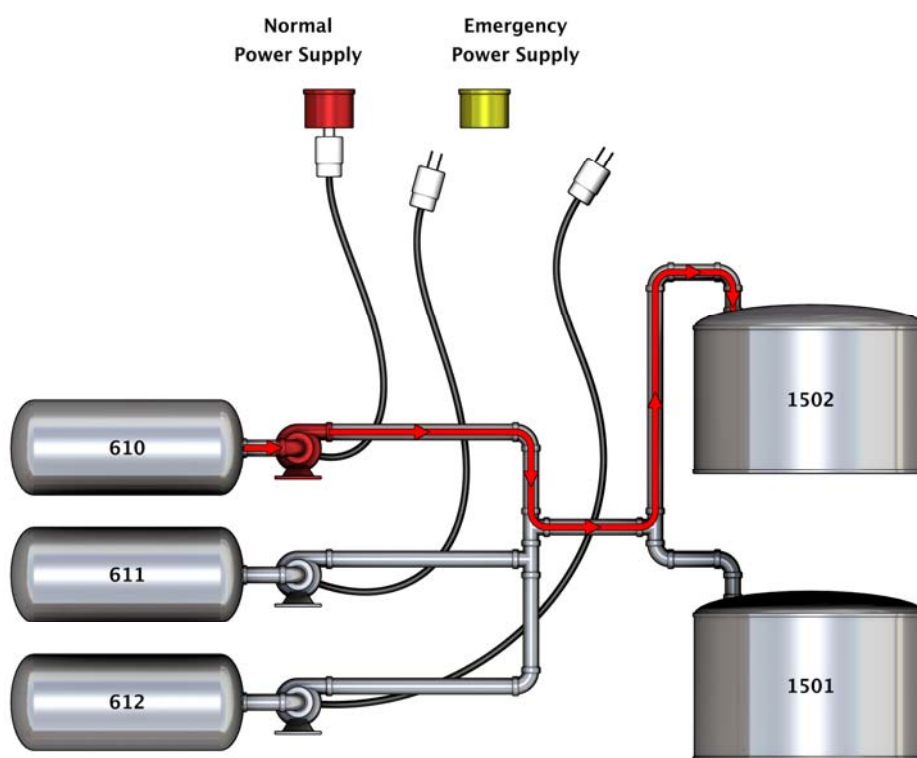


Figure 3. Normal power configuration

⁹ DCS is a digital basic process control system that monitors and controls multiple process inputs and outputs.

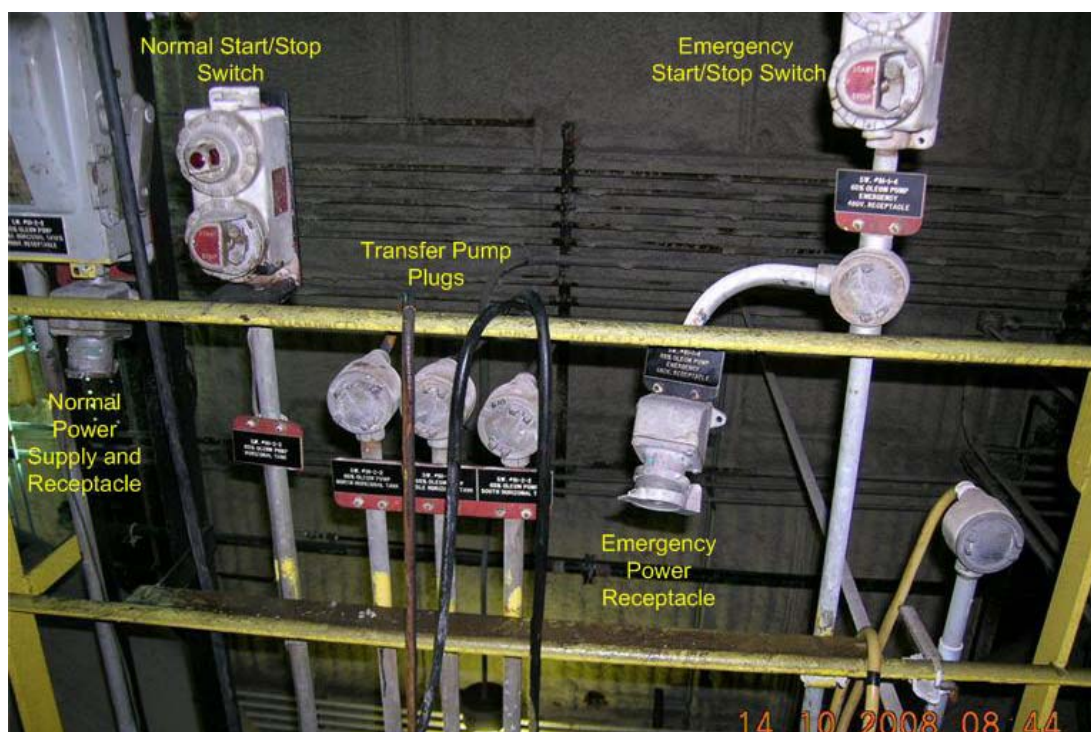


Figure 4. Power supply arrangement

2.2 Emergency Power Supply

Prior to 1980, equipment failures in the oleum storage building affecting the normal power supply interrupted facility operations. Former and current employees stated that power-supply repair parts were difficult to obtain; thus, to minimize production interruptions, the facility¹⁰ temporarily wired an emergency power supply with a separate switch and receptacle. A former operator told the CSB that at the time of this installation, a former supervisor verbally instructed operators to use the emergency power supply to transfer oleum from the pressure vessels to the process tanks. However, the emergency power supply did not incorporate the safety features of the normal power supply. The automatic shutoff that was tied to a high-high level switch¹¹ in the process tanks would not stop a pump powered by the emergency power supply. Therefore, the former supervisor cautioned operators to monitor these transfers closely to prevent overfilling.

¹⁰ At that time, Koppers owned the facility.

¹¹ A high-high level in a storage tank is a point at which the liquid in the tank has reached a dangerously high level and may spill. A high-high level is normally associated with an alarm and an automatic means of shutting down liquid transfer, as opposed to the high level point at which only an alarm is initiated.

Over the nearly 28 years since its installation, the emergency power supply arrangement remained functionally unchanged. The facility did not document the original intent of the emergency power supply in plant drawings¹² or procedures. Post-incident, the current managers, supervisors, and engineers told the CSB that they did not know of the original intent of the emergency power supply or its use in oleum transfer to the process tanks.¹³ At the time of the incident, operators routinely used the emergency power supply on weekends—when supervisors, managers, and engineers were generally not in the facility—to transfer oleum from the pressure vessels to the process tanks.

¹² The piping and instrumentation drawing shows a single power supply for the oleum transfer pumps.

¹³ Many years later, the facility added to the emergency power supply to allow operators to pump from trucks if railcars of oleum were unavailable. However, operators and supervisors from the 1980s and 1990s all stated that trucks were always pressurized with air in the same manner as railcars and were never pumped.

3.0 The Incident

At about 9:45 am on Saturday, October 11, 2008, an INDSPEC shift supervisor called the oleum storage-building operator to the facility to prepare soda ash for the process. The operator arrived at about 11:45 am and began transferring oleum from the pressure vessels to the process tanks, as was customary, before preparing the soda ash.

The operator began pumping oleum to a process tank from vessel 611 using the normal power supply and from vessel 610 simultaneously using the emergency power supply. When vessel 610 ran empty, the operator began pumping from vessel 612 (Figure 2) using the emergency power supply.

At about 2:00 pm, the operator completed soda ash preparation and shut down the soda ash process. He returned to the control room and, using the DCS console, stopped the vessel 611 oleum transfer pump. The transfer pump connected to the emergency power supply remained on, and the transfer of oleum to the process tank from vessel 612 continued. The operator told the CSB that he believed he had shut down the transfer pump connected to the emergency power supply.

The DCS did not display the status of a transfer pump connected to the emergency power supply; only the local start/stop switch could stop a pump powered by the emergency supply.

At 2:13 pm,¹⁴ an alarm beacon indicated a high level in process tank 1502. However, by 2:13 pm, the operator had exited the oleum storage building and the control room; he left the facility at 2:15 pm.

At 2:18 pm, process tank 1502 reached the high-high level setpoint, activating another alarm beacon. By 3:12 pm, sulfuric acid mist began escaping in the area of the tank 1502 conservation vent.¹⁵

Around 4:15 pm, employees saw a white mist escaping the oleum storage building doors and notified the shift supervisor. The shift supervisor, suspecting an oleum leak in the transfer line from the process tank to the process, ordered the transfer line

blown clean. Operators blew the line with pressurized air; however, the release continued and appeared to increase in intensity. Security video from inside the building showed an increase in intensity at 4:21 pm; by 4:29 pm, white sulfuric acid mist was visible outside of the oleum storage building.

Realizing that the release was not from the transfer line, the shift supervisor (acting as incident commander) declared an emergency and ordered a facility evacuation. At 4:55 pm, the facility security guard began notifying the INDSPEC hazardous materials response team. Facility evacuation began concurrent with notification of local residents to evacuate their homes or shelter-in-place.¹⁶ Emergency responders from Petrolia and neighboring towns closed roads leading to the Petrolia valley and walked door-to-door notifying residents.

At 4:58 pm, the shift supervisor instructed INDSPEC responders to spray the oleum building with water from two fire monitors¹⁷ in an attempt to absorb and dilute the sulfuric acid mist. However, the water spray did not lessen the severity of the acid cloud.

To determine the source of the release, an INDSPEC reconnaissance team in Level A personal protective equipment¹⁸ entered the oleum storage building to investigate. The sulfuric acid mist in the building was so dense that the team could only enter a few feet. However, prior to the team's retreat, liquid oleum spilled on them from the top of one of the process tanks.¹⁹ The team concluded that a transfer pump was running and that oleum transferring from one of the pressure vessels had overfilled the process tanks.

The team decided to stop the transfer pump to secure the release but could not reach the local electrical switch room safely because it was flooded with fire

¹⁴ Times in this section were obtained from INDSPEC security camera 3, located inside the oleum storage building above run tank 1502, and security camera 6, located outside of the oleum storage building to the south.

¹⁵ A conservation vent allows airflow (breathing) in a tank while reducing product vapor emissions.

¹⁶ Petrolia volunteer firefighters and police officers notified local residents. Residents in Petrolia and to the south evacuated to the Karns City High School; residents to the north evacuated to the Bruin Community Center.

¹⁷ A fire monitor is a stationary nozzle that directs a spray of water to a specific location.

¹⁸ Level A protection is a fully encapsulated suit with a self-contained breathing apparatus to protect the wearer from chemical exposure.

¹⁹ Oleum spilled from the conservation vent and collected on top of the process tank, eventually spilling over to the floor below.

water. At about 7:00 pm, electricians used a remote disconnect switch to de-energize the oleum storage building and stop the pump. Post-incident data shows that vessel 612 emptied by about 5:50 pm.

Cleanup began after the spilled oleum released the dissolved sulfur trioxide and the sulfuric acid mist dissipated. At about 2:00 am on Sunday, October 12,

air monitoring by the EPA found no trace of vapors from the release. The offsite incident commander declared the emergency over and allowed residents to return home. One emergency responder suffered a minor injury due to sulfuric acid inhalation. No other injuries occurred.

4.0 Analysis

4.1 Control and Alarm System

Each of the five oleum tanks (three pressure vessels and two process tanks) is equipped with two level-sensing devices. The first device continually monitors the oleum level and displays it on the DCS console. The second device²⁰ is a fixed high-high level probe. Each device activates one alarm in the oleum storage building and another on the DCS console. In addition, each high-high level probe on the process tanks activates a switch that shuts off the normal transfer pump power supply.²¹

Although process tank levels are monitored and displayed regardless of which power supply is used, the high-high level probes on the process tanks do not shut off the transfer pump when the emergency power supply is used. Additionally, even though INDSPEC installed the DCS about two years prior to the incident, many years after the installation of the tanks and the level devices, the emergency power supply was not connected to the DCS.

The level sensing devices also activate visual warning beacons above each tank: amber for high level and red for high-high level. In normal practice and in accordance with written operating procedures, operators fill the tanks to the high-level alarm set point, at which they receive visual and audible signals. At the time of the incident, the audible alarm in the oleum storage building was out of service. However, the operator had left the facility and would have been unable to hear the audible signal had it functioned.²²

The DCS console provides operators control and level monitoring capability for a pump connected to the normal supply on the DCS console; it does not provide control or direct indication for a pump powered by the emergency supply.

²⁰ The high-high level device is a capacitance probe-type. Any liquid contact with the probe results in activation of the switch.

²¹ The switch activates independently of the DCS; this is a hard-wired interlock.

²² The CSB found the alarm was out of service for many months and INDSPEC had no process to regularly test the alarm's function.

4.2 Emergency Power Supply Installation

When installed prior to 1980, the emergency power supply enabled the facility to continue operating by transferring oleum to the process tanks when the normal power supply was out of service. At the time of the incident, the label on the power supply read "65% Oleum Pump Emergency 480V Receptacle."²³ Former facility management considered service outages to the normal power supply emergencies due to their potential to halt production.

By installing the emergency power supply without the same safety devices as the normal power supply, the facility traded safety for efficiency. Although a high-high level shutoff, such as the one connected to the normal power supply, could have been added to the emergency power supply, the facility relied on human intervention as a safety measure. Within the hierarchy of controls concept,²⁴ human intervention is less robust than engineering controls such as automatic shutoffs.

4.3 Training and Procedures

According to current and former employees, the normal power supply for oleum transfer malfunctioned about five times between 1980 and the mid-1990s. Operators were required to use the emergency power supply to transfer oleum during these periods.

Operators received only verbal instructions on using the emergency power supply. These verbal instructions were passed down from experienced operators to new operators in on-the-job training. The facility never included the use of the emergency power supply in its written operating procedures for transferring oleum to the process tanks.

Prior to the incident, the facility began the process of updating the written operating procedures. A shift supervisor was responsible for updating the oleum storage building procedures, a process that involved at least one experienced operator. The supervisor instructed the operator to remove out-of-date information from the procedures and add new procedures. At

²³ Operators told the CSB that the labels had never been changed.

²⁴ In the hierarchy of controls, engineering measures are superior to administrative and procedural measures, which are superior to personal protective equipment.

the time of this update, the use of the emergency power supply was neither new nor out-of-date and was not addressed.

4.4 Normalizing the Hazard

When the emergency power supply was originally installed, the facility employed two operators for liquid unloading and storage duties. Often, the operator assigned to the oleum storage building was unable to attend to duties in the building until late in the day because of other responsibilities. The operators developed a work practice in which they used two transfer pumps concurrently (one connected to the normal power supply and one to the emergency power supply) to transfer more oleum to the process tanks in less time. To get their work done in the time allotted, operators used this work practice almost daily, normalizing it. According to a former employee, the former building supervisor was aware of the practice of using two pumps concurrently.

Although the alternate power supply was likely intended to be temporary, the facility replaced flexible electrical cord with wiring in conduit following a safety audit in the 1980s, making the alternate power supply effectively permanent.

In the late 1980s, the facility added a third operator to the area. The presence of a third operator meant that the operator for the oleum storage building would not have to leave the area and could transfer oleum using one pump (with the normal power supply) without falling behind schedule. However, experienced operators continued to train new operators on the use of the emergency power supply.

4.5 Weekend Practice

Shift supervisors typically call operators to the plant on weekends to mix the soda ash solution, which takes about 2.5 hours. While operators prepare soda ash,

they also transfer oleum from the pressure vessels to the process tanks. Up to and including the day of the incident, operators used two transfer pumps (one connected to the normal power supply and the second to the emergency power supply) on weekends to transfer as much oleum as possible during the 2.5 hours (Figure 5).

Operators transferred oleum on the weekends to improve the efficiency of oleum unloading operations on Monday. Operators stated that having at least one pressure vessel empty on Monday morning allowed the incoming oleum storage operator to begin immediately filling the pressure vessel from rail cars. Without room in the pressure vessels on Monday morning, the operator would first need to transfer oleum to the process tanks, delaying the railcar unloading. The emergency power supply eventually came to be used only on weekends, when additional oleum transfer could be accomplished in advance of the normal workweek. This proactive transfer and emptying of the pressure vessels maximized the efficiency of operators' weekend work. Operators used the emergency power supply for nearly 28 years; however, the practice was never identified as a potential hazard.

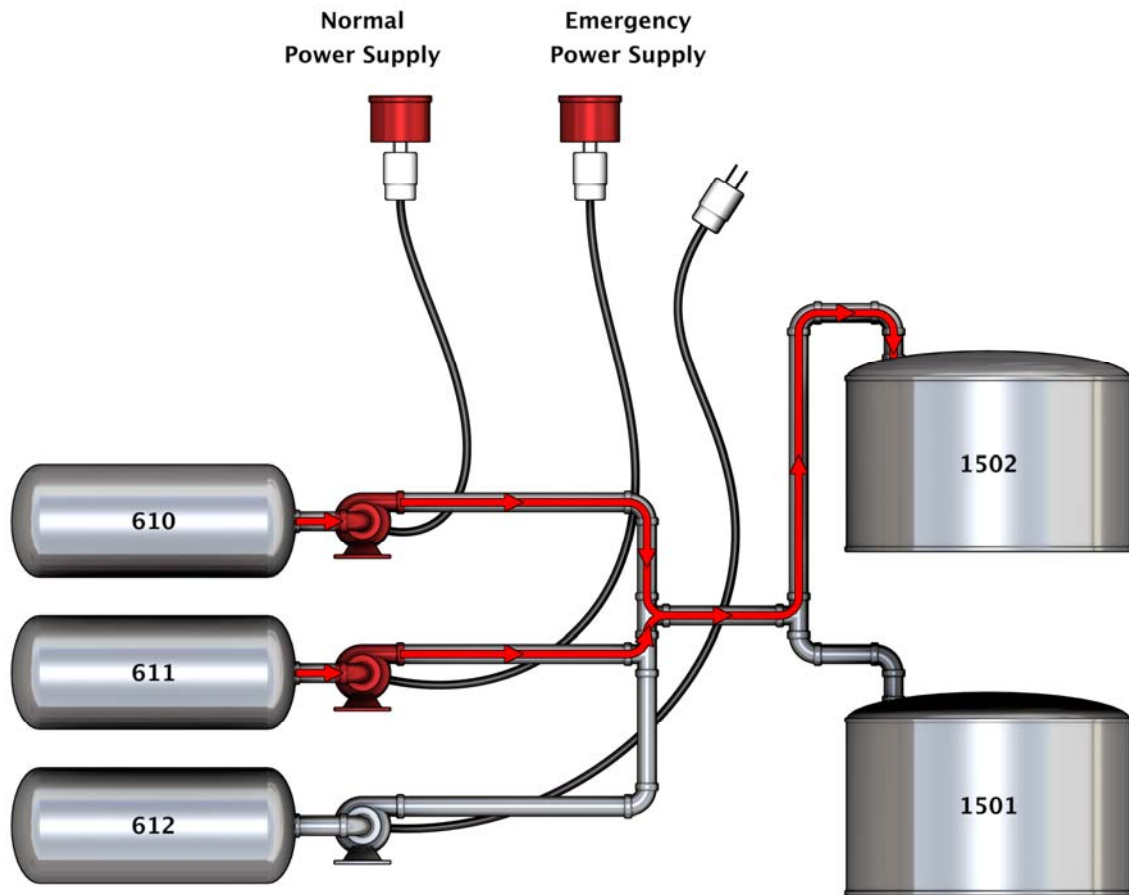


Figure 5. Weekend power configuration

4.6 Process Hazard Analysis

A process hazard analysis (PHA) is a system facilities use to evaluate potential hazards within processes and operations. In general, teams comprising managers, supervisors, engineers, and operators perform PHAs for each functional area of a facility. INDSPEC performed two recent PHAs of oleum storage-building operations.²⁵ In 2005, a PHA team evaluated oleum unloading operations, including storage in the pressure vessels; in 2008, a team evaluated operation of the process tanks. Both PHAs addressed vessel and tank operations including high level, overfill, low level, and overflow into the vent system.

Each oleum storage building PHA team included at least one experienced operator. The CSB interviewed many of the PHA team members and concluded that at the time the PHAs were conducted, only operators were aware of the emergency power supply and its use on weekends. In addition, piping and instrumentation drawings²⁶ and operating procedures did not identify it as an alternate method of transferring oleum to the process tanks.

When INDSPEC conducted these PHAs, operators had used the emergency power supply to transfer oleum for more than 25 years. Operators were aware that the emergency power supply was not controlled by the DCS and that the high-high level switch would not shut down a pump. However, they had been trained by experienced operators on the use of the emergency power supply and believed that using it was safe as long as they closely monitored tank levels.

The safeguards listed in the PHAs for the deviation, “Liquid oleum introduced into vent system by overfilling oleum tanks” are

- Level indication on oleum tanks
- High level alarm
- Operator in attendance

These safeguards, however, all require operator attention and action.

In addition, the PHA discussion of human error safeguards gives equal importance to the high-high level switch, high-level alarm, operating procedures, and operator training. However, only the high-high level switch can reliably perform a transfer pump shutdown regardless of potential human errors.

When an operator inadvertently omits a planned action, it is referred to as a lapse. On the day of the incident, the operator intended to—and thought he had—shut off the pump plugged into the emergency power supply prior to leaving the facility. The PHA teams did not recognize or understand that an operator could potentially suffer a lapse during oleum transfer and not be in attendance to correct it. Details on the emergency power supply had never been captured in standard process safety information such as procedures and drawings. Therefore, the PHA teams did not identify the emergency power supply as a separate means of creating hazardous situations.

²⁵ Both were revalidations of existing PHAs.

²⁶ A single power supply is depicted on the piping and instrumentation diagram.

5.0 Lessons Learned

5.1 Change Management

In the 1980s, the facility changed the structure of the emergency power supply from temporary wiring to permanent conduit. The facility did not evaluate the significance of this change.

Evaluate all changes—even those considered temporary—as permanent, including hazard analysis, procedures, training, and drawings. Establish and enforce time limits for temporary changes.

5.2 Safeguard Evaluation

The facility installed the emergency power supply without the engineering controls that already existed on the normal power supply and without improving alarms and shutdown systems. Although operator action was the sole protection against tank overfill, the facility gave operators only verbal instruction on the use of the emergency power supply.

In the hierarchy of controls, administrative and procedural control ranks below engineering control as a safeguard. Ensure that all modes of operation are equipped with equally robust safeguards for similar hazards.

5.3 Operating Procedures

The facility's storage system design required operators to transfer oleum on the weekend to ensure operations were unaffected during the week. Operators used a work practice developed years earlier to transfer oleum using two pumps concurrently. This work practice was never recorded in written operating procedures.

Work practices can develop that do not reflect written operating procedures. Workers may use alternate practices to streamline tasks. Such alternate practices can introduce potential hazards that have not been formally evaluated. Management must engage operators in every step of procedure development and remain vigilant in evaluating how work is actually performed.

5.4 Process Hazard Analysis

The facility never included information on the emergency power supply in piping and instrumentation diagrams and written operating procedures. PHA teams were therefore unable to evaluate the consequences of emergency power supply use.

The quality of PHAs suffers when piping and instrumentation drawings and procedures are not accurate. Facilities must develop protocols requiring drawings and procedures be updated as soon as changes occur.

6.0 References

American Industrial Hygiene Association (AIHA). *Emergency Response Planning Guidelines*. AIHA Publication No. AEAR05-561. 2005.

National Institute for Occupational Safety and Health (NIOSH). *Pocket Guide to Chemical Hazards*. DHHS Publication No. 2005-149. September 2007.

U.S. Environmental Protection Agency (EPA). Chemical Accident Prevention Provisions, 40 CFR 68 Subpart F, Regulated Substances for Accidental Release Prevention.

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