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Learning from what went wrong—two case studies

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Abstract

Safer design of process equipment can protect against unexpected events. Two case studies involving the design of a process vessel and the subsequent events will be reviewed. One case study will show how the original design minimized equipment damage from an operational error, and how additional safeguards will prevent recurrence. The second case study will show that over time small process changes can lead to an unexpected chemical reaction that results in a vessel rupture. We will also cover the additional safeguards added to prevent recurrence.

Keywords: Overpressure; Operator error; Maleic anhydride; Thermal decomposition; Hydrogen

1. Case study no. 1: hydrogen contamination of a nitrogen system

1.1. Event description

A polymer plant was shut down and was being prepared for maintenance. Hydrocarbon feeds, including the 350 psig hydrogen, were isolated from the process. Nitrogen at 90 psig was connected to the process by procedure to purge residual hydrocarbons out of the piping system and into a vent system. During the next 2 hours, combustible gas analyzers (CGAs) on enclosed cooling water surge tanks and the vents on several other vessels occasionally indicated the presence of flammables. Operators and supervisors responded to those alarms. Manual checks by personnel with portable CGAs did not detect any hydrocarbons in the vessels and no hydrocarbon odors were detected. About 2.5 hours from the start of purging, an explosion occurred in the final degasser and its auxiliary equipment. Automatic sprinklers tripped which extinguished the fire in the degasser. The plant emergency response team deployed fire hoses and eliminated hot spots. No one was injured. The degasser internals sustained significant damage but no appreciable damage was done to the 24,000 gallon vessel. Several auxiliary pieces of equipment were also damaged.

The final degasser normally contained polymer powder in an air atmosphere. Essentially all volatile hydrocarbons are removed from the powder before entering the final degasser. A blower recycled and purged air through the vessel to remove the small amount of residual hydrocarbons to a vent system. As an added precaution, two permanent redundant combustible gas analyzers in the recycle line were calibrated to alarm at 25% of the lower explosive limit of the process gas. The blower had been shut down for the maintenance activity that left stagnant gas by the CGA sensor. The final degasser operated about 1 psig pressure but was rated for 17 psig. Powder is transferred from the last degasser through a pressure lock and a pneumatic transfer system to product handling operations for shipment. Because of the potential for a dust and air mixture in the degassing system, or the inadvertent migration of hydrocarbon vapors entering the degasser from upstream processes, the degassing vessel had two, 42 in. diameter explosion panels set at 3 psig on opposing sides of the vessel (see Fig. 1).

An investigation initiated immediately after the area was declared safe to enter discovered that a nitrogen purge hose had been connected to the wrong side of the hydrogen block valve. This allowed 350 psig hydrogen to flow into the 90 psig nitrogen system. The hose was immediately valved off and disconnected and the nitrogen system was purged and cleared of hydrogen. There was no check valve in the temporary nitrogen connection. At the time of the event, the procedure did not require a backflow preventer because the process was depressured.

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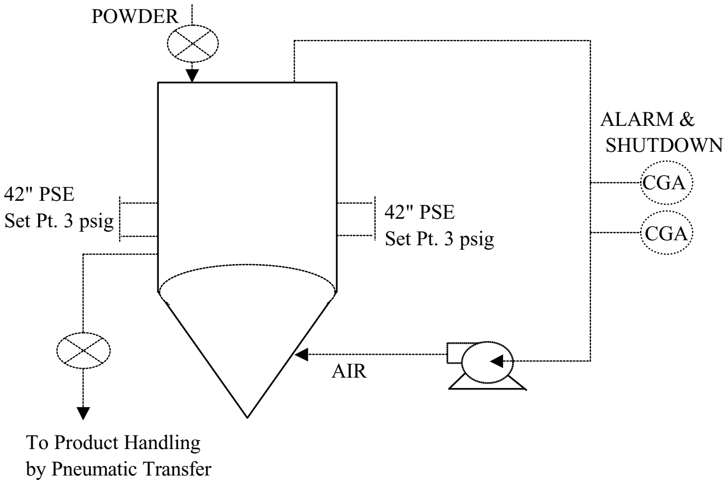

Fig. 1. Degasser piping diagram.

Hydrogen has very wide flammable limits (4–75%) and one of the lowest minimum ignition energy requirements (0.01–0.02 mJ). The normal hydrocarbon in the powder has flammability limits of 1–7%. It is believed that hydrogen backed into the nitrogen header, entered the degasser through upstream purging, and found an ignition source. Because of the wider flammability limits and lower minimum ignition energy for hydrogen, it is believed a static charge in the powder ignited the gas.

The powder is very coarse and not easily susceptible to dust explosions. Product quality requirements prevent the accumulation of any fines. Housekeeping in the production area is excellent and there were no accumulated solids that could have been shaken loose by the initial explosion to propagate a more serious event. Small amounts of unburned or charred powder were found in the vessel after the fire. Damage to the vessel was minimized because much of the force from the explosion exited the vessel through the explosion panels. Movement of the vessel by the explosion and exiting gases caused damage to auxiliary equipment. Some structural steel supports near the discharge of the explosion panels sustained enough damage to require replacement. The damage was repaired in the normal shutdown window.

1.2. Improvements made and lessons learned

Purging of equipment occurs routinely through temporary lines. Trained and conscientious operators still have the potential to make mistakes. In this incident, the operator removed a plug from the wrong drain valve and installed a fitting to allow nitrogen to be connected (see Fig. 2).

With the hydrogen valve locked out, the operator was to purge the downstream header so that the Figure 8 blind could be rolled to isolate the process for confined space entry downstream. This incident occurred because sufficient controls were not in place to protect the system from a human error. The event was mitigated because of the fixed automated sprinkler protection and the relief panels. Designing mitigating controls into the original design of a process will significantly reduce damage from an unforeseen operating error.

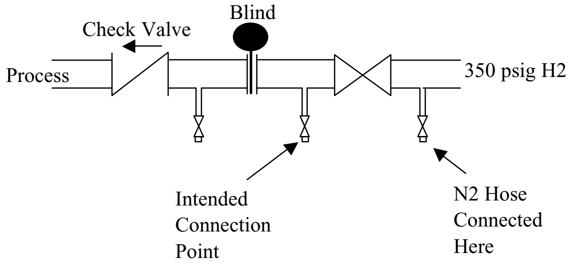

Fig. 2. Piping diagram of nitrogen purge connection points.

1. Procedure was implemented to require force-loaded check valves for backflow prevention for any temporary connection to piping that contains flammables. The check valve must be rated for the highest process pressure that can be seen.
2. Personnel access restrictions were increased at the blowout panels.

2. Case study no. 2: catastrophic failure of maleic anhydride storage tank

2.1. Event description

In this event, maleic anhydride (MA) was stored molten in an 8000 gallon tank with a maximum allowable working pressure of 50 psig and a relief valve set at 50 psig. MA has a melting point of 52 °C. The tank and piping were kept hot with temperature limited electrical tracing set at 75–80 °C. The line from the storage tank to the exchanger was heated in two sections with two electric heat tracing circuits. The piping system included a molten bulk truck unloading line, a centrifugal pump taking suction from the bottom of the

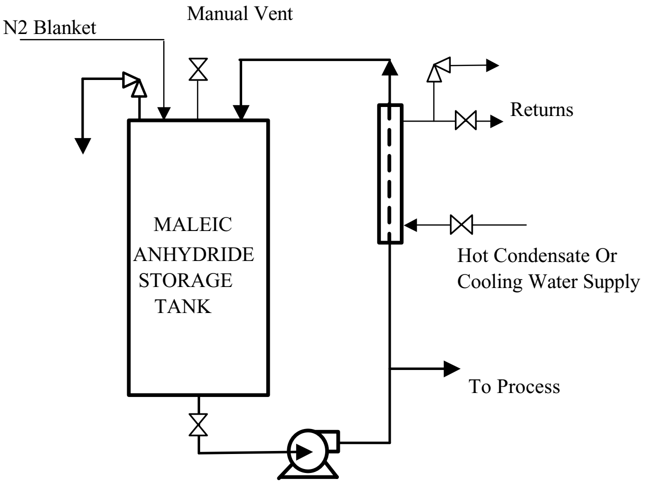

Fig. 3. Simplified diagram of maleic anhydride storage tank.

tank and a discharge line that split with one line going to the process and the second stream being recycled back to the storage tank. MA was continually recycled to keep the storage tank uniform and to provide a constant feed to the process. A stainless steel annular pipe heat exchanger had been added after initial plant startup to the recycle line to remove heat buildup in the tank from the energy added by the recycle pump. The exchanger was capable of using either hot condensate on startup or cooling tower water to remove excess heat during normal operation. The tank had a nitrogen blanket (see Fig. 3).

Operation problems resulted in plugging of the MA process feed line. Attempts to unplug the process line were unsuccessful and required shutdown of the pump. When operations attempted to restart the pump, they found that the recirculation line had also plugged.

Efforts to unplug the recycle line focused on locating a suspected cold spot in the piping. Operations had determined that the piping around the pump was cool to touch but the heat tracer controllers indicated the line temperatures were 85–150 °C. The electric tracing controllers were checked and found to be working correctly so the set point for the colder section of pipe was increased. Investigations later showed the controls for the two tracers had been crossed and one section of tracer had been replaced with standard electric tracing that was not temperature limiting. This would allow excess power to heat the line. It is believed that the temperature in the piping reached the thermal decomposition temperature for MA (253 °C). This generated significant pressure from the decomposition gases generated and ruptured the exchanger annulus creating a hole in the inner pipe that was unknown to operations.

Numerous times operations opened and closed the hot condensate supply to the exchanger. Unknown to the operators, each time the condensate valve was opened to heat the exchanger, water entered the storage tank. The water initiated an exothermic hydrolysis reaction that converted some of the MA to maleic acid. Since maleic acid has a melting point of 137 °C, this caused additional plugging problems.

After 2 days, the crossed wiring on the piping heat tracers was identified and corrected. Operations noticed that the storage tank temperature had slowly increased from 90 to 160 °C and assumed the temperature increase was related to a tracing problem and having the temperature probe too close to the tracing. This was re-enforced later that day when the electric tracing contractor confirmed a tank heat tracer problem. The exchanger leak was detected by operations and it was locked out. Operations started developing plans to drain and dispose of tank contents the next day. Previous experience with small amounts of water contamination in tank trucks and other containers had resulted in plugging problems from the formation of the acid but no significant temperature rise had ever occurred.

The next morning the storage tank temperatures were reading above 200 °C when the relief valve opened. An emergency was declared and the emergency response team immediately applied water spray to contain vapors. All electric power was disconnected from the tank and piping, and a manual vent was opened on top of the tank. Actual pressure in the tank was not available because the tank pressure gauge pegged at 70 psig. White vapor exited the relief valve and vent. Due to the venting, pressure reduced in the tank and the relief valve reseated. The manual vent rate appeared to diminish. Suddenly a shrill sound was heard from the relief valve and the atmospheric vent rate increased and the discharging vapors turned from white to black. The insulation bands on the tank began to pop off and personnel were notified to clear the area. Minutes later the tank ruptured throwing debris up to 500 ft away. Significant damage to area piping was sustained. No fire occurred. There were no serious injuries.

2.2. Improvements made and lessons learned

Even though operations personnel were aware of the potential hazard of decomposition of MA, they failed to recognize that the hydrolysis reaction and not the heat tracing was causing the temperature to rise. It is theorized when the unreacted water was all vented out of the tank, the heat from hydrolysis increased the MA temperature to the decomposition reaction temperature. System design and previous experience clouded the hazards from personnel. Process heating media were designed to be failsafe and prevent heating MA anywhere close to the decomposition temperature. Cold spots in the line were usually caused by electric tracing problems. When water contamination had occurred in other MA vessels, the quantity was not enough to generate the heat to reach the decomposition temperature. The small amounts of water converting MA to maleic acid created a nuisance operability problem usually solved by a shutdown and several days of cleaning the system.

This incident occurred for the following reasons.

- The vessel pressure relief system was not designed to handle the decomposition reaction of MA because the following controls were deemed adequate:
  - design and operating temperatures were significantly below decomposition temperatures;
  - heat tracing systems were designed to be failsafe.
- Heat tracing had been changed so a section was no longer failsafe.
- The controllers were crossed during maintenance. When the MA flow stopped, the tracers overheated the MA, triggering a decomposition in the pipe and a rupture in the exchanger annulus.
- A stainless steel exchanger was added after the initial installation that was susceptible to chloride stress cracking.
- The exchanger provided a single source failure to introduce water into the MA to initiate the exothermic hydrolysis reaction that lead to the decomposition reaction.

As a result of this incident, the following changes were implemented.

1. The piping design was modified to eliminate the single source failure for inadvertent water addition from the exchanger.
2. The replacement relief device was designed to protect the vessel from the exothermic decomposition reaction.
3. Pressure indicator with greater range was added to the vessel and temperature indication was modified so that there was no interference from the electric tracing.
4. The electrical tracing was replaced with temperature limited tracing. The MOC process was improved in electrical maintenance.
5. Critical electrical wiring and safety notes are now denoted on process and instrumentation diagrams.
6. The set point for the electric tracing was lowered to 65 °C.
7. An independent high temperature shutdown interlock set at 150 °C was connected to each heat tracer.