

Safety Bulletin

U.S. Chemical Safety and Hazard Investigation Board



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FIRE AT PRAXAIR ST. LOUIS

DANGERS OF PROPYLENE CYLINDERS IN HIGH TEMPERATURES

Summary

When exposed to high temperatures and direct sunlight, propylene cylinders can spontaneously vent through their relief devices, in turn releasing propylene, which when ignited, can heat surrounding cylinders and cause them to vent, creating a domino effect that spreads the fire. This is what occurred on June 24, 2005 at Praxair's gas filling and distribution facility in St. Louis, Missouri. A small fire from one propylene cylinder spread to others and then to propane and acetylene cylinders. Exploding cylinders flew up to 800 feet, damaged property, and started fires in the community. The fire could not be extinguished until most of the flammable gas cylinders were expended.

The U.S. Chemical Safety and Hazard Investigation Board (CSB) issues this *Safety Bulletin* to focus attention on the propylene gas cylinder hazards that contributed to the fire and explosions at the Praxair facility and specific actions that propylene gas vendors can take to prevent similar incidents, which include:

- Installing deluge systems or fixed fire nozzles to cool cylinders in case of a fire;
- Providing barriers to limit fire spread; and
- Using flammable gas detectors in storage areas to provide early detection of venting cylinders.

- ***A small fire from one propylene cylinder spread to others and then to propane and acetylene cylinders. Exploding cylinders flew up to 800 feet, damaged property, and started fires in the community.***

Figure 1. Fire at Praxair St. Louis

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St. Louis Facility

The St. Louis Praxair Distribution site fills and distributes liquefied and compressed gas cylinders, rents welding machinery, and sells welding supplies. At the St. Louis facility, Praxair has about 30,000 compressed gas cylinders containing oxygen, nitrogen, propane, propylene, acetylene, carbon dioxide, helium, and other specialty gases onsite. The facility employs about 70 and is located in a commercial and residential area near Lafayette Square.

Praxair divided the cylinder storage into “full” and “empty” or “returned” sections. The “returned” section, where the fire originated, is for cylinders returned for refilling, which may not always be empty when returned.

Incident

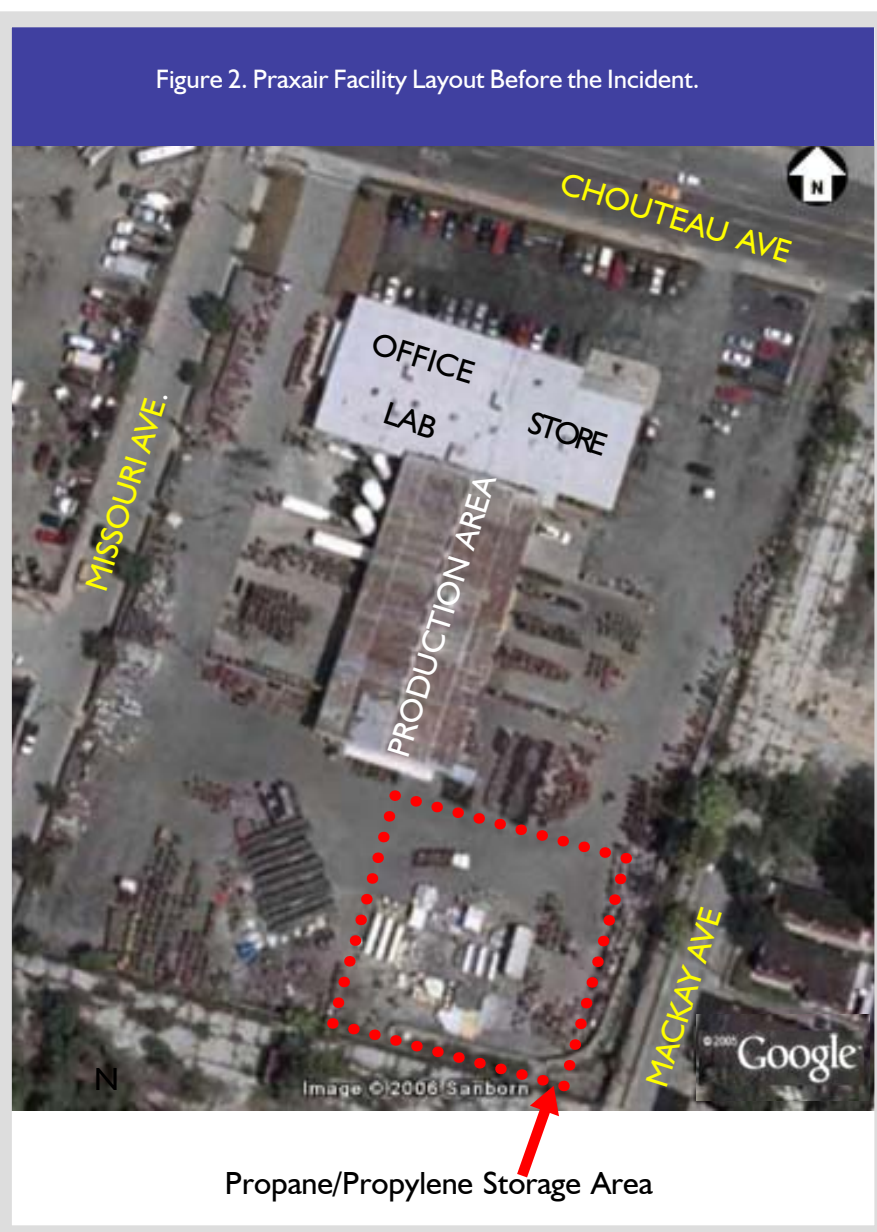
Incident Description

St. Louis was experiencing a heat wave with bright sunlight and temperatures reaching 97°F (36°C) on June 24, 2005. Praxair operations proceeded normally during the morning and early

afternoon; however, about 3:20 pm, a technician retrieving cylinders from an outside storage area saw a ten-foot high flame coming from a cylinder (Figure 3) and activated the fire alarm. Security camera video from the facility shows the release and ignition of gas from a cylinder in the propylene return area.

● ***[A]bout 3:20 pm, a technician retrieving cylinders from an outside storage area saw a ten-foot high flame . . .***

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 good practices for prevention. All reports include safety recommendations when appropriate. CSB Investigation Digests are plain-language summaries of Investigation Reports.



As workers and customers evacuated, the fire spread to adjacent cylinders. Security camera video shows nearby cylinders igniting in the first minute. At 2 minutes, cylinders begin exploding, flying into other areas of the facility, and spreading the fire (Figure 4). After 4 minutes, the fire covers most of the facility's flammable gas cylinder area and explosions are frequent.

Emergency Response

The St. Louis Fire Department arrived at about 3:35 pm; by this time, a large number of flammable gas cylinders were already involved in the fire. With explosions propelling cylinders in all directions inside and outside the facility, firefighters set up a five-block perimeter, evacuated local residents, directed a water stream on the fire, and extinguished secondary fires started by cylinders propelled offsite. The fire was finally controlled at about 8:30 pm.

Community Impact

Dozens of cylinders and cylinder parts were propelled into the community and were found on sidewalks, front yards, backyards, courtyards, parking lots, and under cars. Damage included a burned-

Figure 3. Initiating Event (from Praxair security camera)



Figure 4. Spreading Fire (three minutes after ignition)



With explosions propelling cylinders in all directions . . . firefighters set up a five-block perimeter, evacuated local residents, directed a water stream . . .

Figure 5. Community Impact



out empty commercial building, fire-damaged cars, a three-foot hole in the wall of one residential building, broken windows, and other destruction to residential and commercial buildings. Cylinder parts traveled as far as 800 feet from the area of the explosions (Figure 5). The fire plume spread asbestos¹ from ruptured acetylene cylinders over a 1/3-mile wide and 1-mile long area.²

The St. Louis Chief Medical Examiner attributed the death of one St. Louis resident to an asthma attack triggered by noxious smoke and fumes from the incident.³

Facility Damage

While the facility was damaged extensively by fire and water, 22 employees and two customers evacuated safely in accordance with Praxair's procedures. A corner of the main production building and store area was heavily fire-damaged. Inside, the office and store areas were water- and smoke-damaged. In all, the fire consumed nearly the entire inventory of flammable gas, or about 8,000 cylinders (Figure 6).

¹ Acetylene cylinders are filled with a porous solid material, which in older cylinders, may contain asbestos.

² Following the incident Praxair contracted a cleanup of the asbestos which the Missouri Department of Natural Resources monitored.

³ From report of the St. Louis Medical Examiner, Case Number 2005-2061.

Figure 6. Facility Damage



Incident Analysis

Incident Scenario

The CSB used physical evidence, surveillance video recording, interviews, and information from Praxair's internal investigation to establish the likely failure sequence:

- Direct sunlight and radiant heat from asphalt paving heated returned propylene cylinders;
- High ambient temperature limited natural air-cooling of the cylinders;
- The returned cylinders, containing less gas than full cylinders, heated at a faster rate than full cylinders;
- As the cylinder wall temperatures rose, the internal pressures increased causing the relief device on a cylinder valve to open and vent propylene;
- The venting propylene ignited (most likely from a static discharge) at about 3:20 pm;
- An adjacent cylinder, further heated by the fire, released propylene, and caught fire;
- An employee saw the fire and activated the fire alarm;

- All 22 employees and two customers evacuated;
- The growing fire heated additional cylinders, which released more propylene into the fire;
- The fire's intensity continued to raise cylinder temperatures, softening the steel and rupturing the cylinders;
- The fire spread to a group of acetylene cylinders;
- The liquefied petroleum gas⁴ (LPG) area of the facility became fully involved in the fire;
- Ruptured cylinders (acetylene, propane, and propylene) rocketed into the community, damaging buildings and starting several vehicle fires;⁵
- St. Louis Fire Department arrived at about 3:35 pm, established an unmanned water spray on the fire, and retreated to a safe distance. The fire department did not actively fight the main fire due to the danger of rocketing cylinders;
- The Fire Department gained control of the fire at about 8:30 pm, after the fire had consumed most of the flammable gases onsite.

⁴ Liquefied petroleum gases (LPGs) are gases that are liquefied by applying pressure. Common LPGs include butane, propane, and propylene.

⁵ A majority of the cylinders that ejected from the site were acetylene cylinders.

Similar Incidents

CSB found three recent incidents similar to the St. Louis fire. They include:

- Air Liquide, Phoenix, Arizona – June 1997;
- Airgas, Tulsa, Oklahoma – August 2003; and
- Praxair, Fresno, California – July 2005.

These events occurred in gas repackaging cylinder fill plants on days with air temperatures above 100°F (37°C)⁶ and in an area with propylene cylinders.⁷

On June 18, 1997, air temperatures in Phoenix, Arizona reached 108°F (42°C). At about 4:30 pm, propylene was released from cylinders and/or tanks at an Air

Liqueide gas repackaging plant; moments later, the propylene ignited. The fire spread to adjacent cylinders, followed by explosions that further damaged the facility. Investigation reports concluded that the incident resulted from the release of propylene close to LPG cylinders and bulk tanks and that high temperature was a contributing factor.

On August 18, 2003 air temperatures reached 100°F (37°C) in Tulsa, Oklahoma. At about 4:30 pm, a vapor cloud of propylene that had formed around cylinders in the yard ignited, spreading fire around the Airgas gas distribution plant. As in the St Louis incident, cylinders exploded and flew into the community, damaging cars and homes (see Figure 7). Tulsa Fire Department investigators

Figure 7. Tulsa Damage

Photo courtesy of Tulsa Fire Department



⁶ Air temperature data from the nearest National Weather Service reporting station.

⁷ Identified in the fire department or company investigation report.

concluded that although the official cause is undetermined, the most likely cause was “propylene venting due to the prolonged exposure to excessive heat.”

Comparing Propylene and Propane

This safety bulletin describes several gas repackaging facility fires that likely began with a spontaneous propylene release, similar to the fire in St. Louis, and that occurred since 1996. Although about 1,000 times more propane cylinders are in service than are propylene cylinders,⁸ CSB found gas repackaging facility fires that began with a propane release do not occur with significantly greater frequency. To understand why, CSB compared propylene and propane cylinder characteristics.

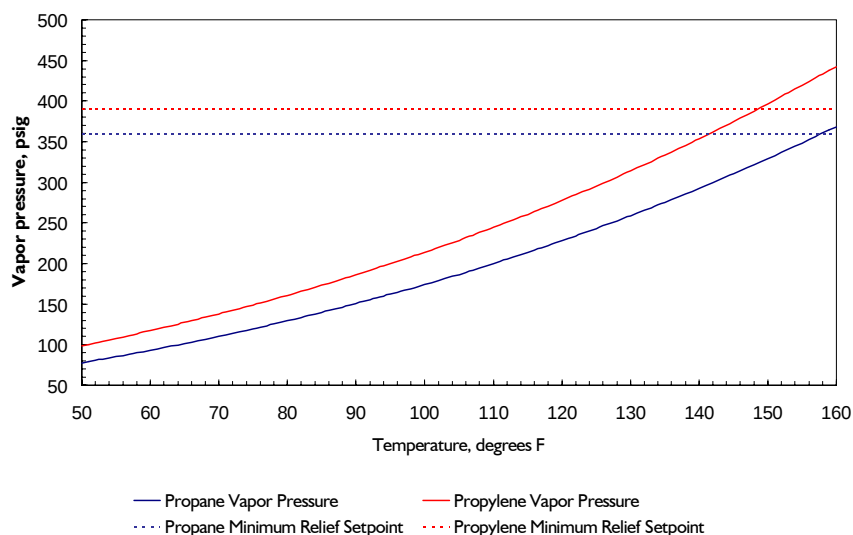
Propylene and propane have similar physical properties; both are liquefied petroleum gases and use the same cylinders and relief device standards. A physical property, known as the vapor pressure,⁹ determines pressure in the cylinder.

Propylene and propane cylinders are manufactured to U. S. Department of Transportation (DOT) standards.¹⁰ The DOT standards require that each cylinder be equipped with a pressure relief device that meets the requirements of Compressed Gas Association, Inc. (CGA) Pamphlet S-1.1, “Pressure Relief Device Standards – Part 1 – Cylinders for Compressed Gases, 2001, Ninth Edition.”¹¹ CGA Pamphlet S-1.1 specifies a CG-7 type relief valve for both propylene and propane cylinders. Pamphlet S-1.1 also specifies the set point of the relief valve. Figure 8 shows the vapor

pressure curves and minimum relief valve setpoints for propylene and propane.

Following several of the fires described, including the St. Louis fire, the affected companies investigated the performance of the propylene cylinders CG-7 relief valves. In 2003, Battelle¹² released a report, “Testing and Assessment of CG-7 Pressure Relief Valve and Propane Cylinder Performance” that documented the results of a study it performed for the National Propane Gas Association. The companies’ investigations and the

Figure 8. Propane and Propylene Vapor Pressures



⁸ The propane industry estimates that 50 million propane cylinders are in use nationwide. CSB has estimated that the number of propylene cylinders in use is about 50,000.

⁹ Vapor pressure is the pressure exerted by a vapor in equilibrium with its solid or liquid phase.

¹⁰ Cylinder standards can be found 49 CFR part 173.

¹¹ The DOT standards exempt users from complying with paragraph 9.1.1 of CGA pamphlet S-1.1, which requires that relief valves be replaced or recertified every 10 years.

¹² Battelle is a non-profit global science and technology enterprise that develops and commercializes technology and manages several national laboratories for the U.S. Government.

Battelle report document variability in the opening pressure of relief valves in service, which found that a significant number open below the minimum pressure required by CGA pamphlet S-1.1. One company study and the Battelle report document a decrease in set pressure for subsequent valve openings after the initial opening.

Although the performance of the CG-7 relief valves appears to be similar for propylene and propane, spontaneous releases leading to large facility fires have occurred primarily with propylene even though about 1,000 times more propane cylinders are in service than propylene cylinders. The propylene fires can be attributed to the greater margin provided in standard propane cylinders between the vapor pressure of propane and the minimum set pressure of the relief valve. Table 1 lists the temperature for various pressures in both propylene and propane cylinders.

As Table 1 shows, propylene relief valves may open at lower temperatures than propane.

Best Practices for Cylinder Storage

National Fire Codes, CGA's "Safe Handling of Compressed Gases in Containers," and company standards provide general guidelines for storing cylinders outdoors:

- Ensure the pressure relief valve is in direct communication with the vapor space;
- Use a well-ventilated area away from oxidizers, open flames, sparks, etc.;
- Post "No-Smoking" signs;
- Post hazard class or name of gases on containers;
- Group by hazard class;
- Protect from objects that will damage the metal surface – not near elevators, walkways, platform edges, or below heavy moving objects that may fall;
- Protect from tampering;

- Avoid prolonged exposure to a damp environment (graded surface prevents water accumulation); and
- Do not obstruct exit routes.

Three additional best practices are relevant to the incidents discussed in this safety bulletin that gas repackaging facilities should evaluate and implement as appropriate: fire mitigation, fire barriers, and gas detection.

Fire Mitigation

Exploding and rocketing cylinders put fire fighters at risk when attempting to extinguish a gas repackaging plant fire. Fixed fire protection such as fire monitors, deluge, or sprinkler systems can immediately cool cylinders reducing the likelihood of additional cylinder releases, fire spread, and off-site consequences.

Fire Barriers

Using barriers in storage areas can contain exploding cylinders and limit the spread of the fire in the first critical minutes before firefighters arrive.

Gas Detection

Area flammable gas monitors can detect releases. Detection of flammable gases may allow safety systems (such as alarms and deluge) to activate before ignition, reducing the likelihood of uncontrolled fires.

Table 1. Pressures and Temperatures for LPG Cylinders

	Propylene		Propane	
	Pressure, psig	Temperature, °F	Pressure, psig	Temperature, °F
Cylinder Service Pressure	260	115	240	124
Minimum Relief Setpoint	390	149	360	158

Lesson Learned

The lesson learned from these fires can help similar facilities avoid damaging incidents. *High ambient temperatures, in combination with low relief valve opening pressure, increase the risk of catastrophic fires at facilities handling propylene cylinders.*

Adopting best practices for storing and handling propylene cylinders can reduce this risk at gas distribution facilities. Revising current practices to provide a greater margin between the minimum relief opening pressure and the vapor pressure of propylene will reduce the risk even when best practices are not followed.

- ***High ambient temperatures, in combination with low relief valve opening pressure, increase the risk of catastrophic fires at facilities handling propylene cylinders.***

Recommendations

Compressed Gas Association (CGA)

2005-I-MO-R1

Communicate with your members who operate gas repackaging facilities the details of this incident and the best practices for handling and storing cylinders.

2005-I-MO-R2

Revise CGA standards for the CG-7 relief valves used in propylene service to require:

- 1) a greater margin between vapor pressure and relief valve setpoint (similar to propane); and
- 2) that valves be capable of multiple operations within the specified setpoint tolerance or be furnished with an indicator that alerts users that the valve has operated.

- ***Revising current practices to provide a greater margin between the minimum relief opening pressure and the vapor pressure of propylene will reduce the risk even when best practices are not followed.***

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