Chemically Speaking LLC

First Responder Assessment of Acetylene Cylinders

Rev. Aug 2021

Acetylene cylinders have unique hazards that an emergency responder must consider in a response.

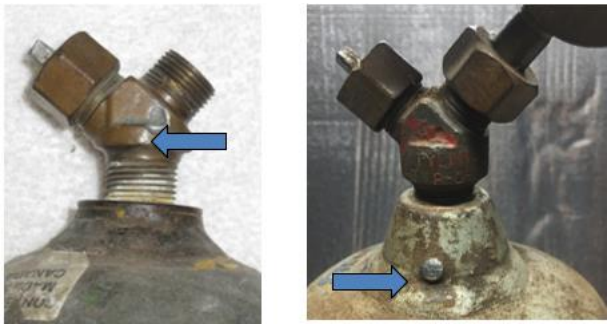
Key Facts

C_2H_2 is a triple bond chemical compound that can decompose to form hydrogen and carbon releasing a lot of energy once ignited without the need for any oxygen to be present. This energy can cause more acetylene to decompose causing the ultimately causing the cylinder to violently rupture and BLEVE. This can be a delayed reaction of a few hours and in rare cases 24 hours.

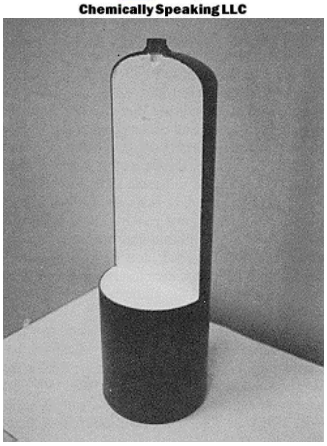
Lighter than air (0.91). Can accumulate in ceiling and suddenly ignite due to disturbance from a hose stream bringing the vapor down to an ignition source. (Conestoga Canada incident)

DOT (ICC old) Specification 8 or 8AL cylinders can only contain acetylene. They are carbon steel with PRDs (fusible 212°F) on the shoulder of cylinder and also on the bottom of the cylinder. Most large cylinder have 2 on the shoulder and 2 on the bottom.

Small cylinders (MC and B) might only have the PRD drilled into the side of the valve.



The cylinders are also filled with a solid porous mass that acts as a heat absorber to quench the heat from a decomposition reaction in order to stop it from progressing.



Most porous masses were previously made from asbestos since it is much more effective in controlling the decomposition due to superior physical characteristics. The porous mass is now made with a clay material with many microcavities. When a cylinder ruptures, all of the porous mass will be propelled out of the cylinder contaminating the area if it contained asbestos.

The acetylene is dissolved in acetone or DMF that is absorbed in the porous mass. Pressure of a full cylinder is 250 psig. Acetylene must not be handled above 15 psig in use as it can violently decompose at pressures above this. This decomposition can transition into a detonation in improperly design systems or cavities.

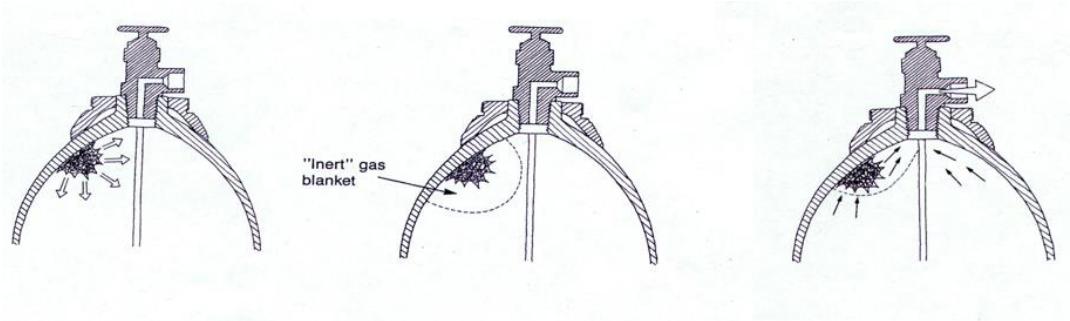
When the acetylene is used, it desorbs from the acetone or DMF. This is why it is an urban legend that a acetylene cylinder that is lying horizontal is unsafe. It is because if it is used while horizontal the acetone or DMF also comes out creating a smoky flame. It should be stood vertical and allow 10-15 minutes for the acetylene and acetone or DMF to equilibrate before using.

Unlike liquefied compressed gases, the cylinder frostline is not a good indicator of cylinder contents since is reflects the cold acetone or DMF not the acetylene. The cylinder in the incident below is close to 0 psig.

Cylinders in which the PRD has melted and the gas is on fire, should be allowed to burn in place. Never extinguish the fire. This will not be effective and could cause a safety problem due to an explosive environment being created. Even in open air, acetylene/air mixtures can detonate.

The decomposition reaction releases tremendous amounts of energy and may generate temperatures between 5072° and 5252° F. When the decomposition takes place in a cylinder with the valve closed the byproduct hydrogen creates an “inert” blanket around the area slowing the decomposition by starving it

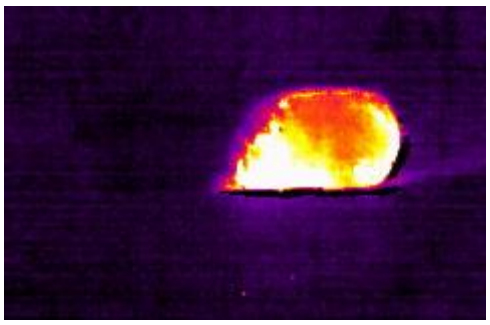
of acetylene. Absolutely no attempt should be made to reduce the pressure inside it by opening the cylinder valve, since to do so would be to set up a motion inside the cylinder which would draw fresh gas through the area of decomposition adding fuel to the decomposition. This was confirmed by Federal Institute of Material Research and Testing in Germany (BAM) testing.



The decomposition becomes dangerous when the porous mass has shrunk or been damaged creating a void where the decomposition can continue uncontrolled. Since the reaction requires fresh acetylene the reaction rate is slow in the beginning since it relies on gas diffusion to bring in more acetylene to decompose. As it continues the temperature increases causing a larger void as well as increasing pressure in the cylinder. This continues until the cylinder ruptures which can sometimes be 24 hours after the reaction had been initiated. Firefighters have been injured or killed after the fire has been extinguished. This is why special ER procedures are in place for acetylene cylinders worldwide.

Testing has shown that cooling with a water spray for an hour is effective in quenching the reaction.

The following thermal imaging picture is an acetylene cylinder lying on its side with the valve pointed to the right. The hose stream had just been turned off and the top of the cylinder (right) dried in secs. The pressure buildup caused the cylinder to rupture at the top. The fusible metal (212^{o}F) PRDs remained intact despite the pressure.



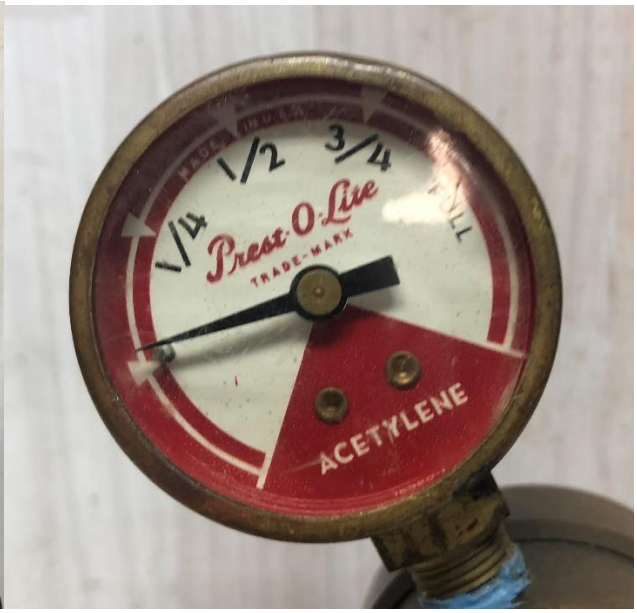
Leaks

It is dangerous to pressurize acetylene above 15 psig, this is why DOT specifically prohibits the use of a cylinder containment vessel in 49CFR173.3(d) since the cylinder is pressrized to 250 psig when full. The same is true for capping kits like the Cl_2 A kit. It is better to allow it to leak until empty or to flare it.

Acetylene is generated from calcium carbide which has high levels of arsenic, phosphorus and sulfur impurities. The arsine, phosphine or hydrogen sulfide will peg any H_2S gas sensor. The garlic odor is the arsine and/or phosphine.

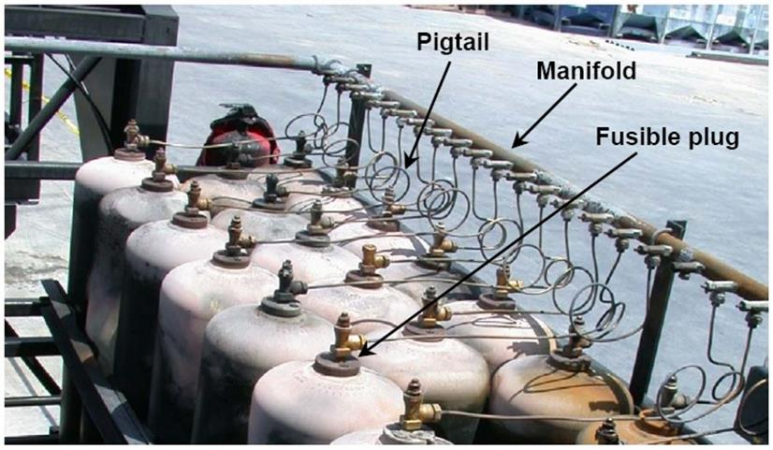
How much is in the cylinder?

The only way to determine how much is in the cylinder is using a pressure guage from an acetylene regulator. Weight is not accurate since the weight of the acetone or DMF is not known. Typically it will be marked at full (250 psig) ¾ (188 psig) ½ (125 psig) ¼ (63 psig) @ 70°F. Higher temperatures will increase the pressure.



Mobile Acetylene Trailers (MATS)

To supply large volumes of acetylene for a cylinder fill or chemical manufaturing facility, MATS are used. These are open trailers with multiple acetylene cylinders mounted and attached to a common piping system.



These have been involved in a number of significant facility or motor vehicle incidents. These must be approached with extreme caution as there can be multiple cylinder failures and fire. No effective method has been developed for these incidents other than flooding quantities of water from a distance to cool and prevent more cylinders from rupturing.

Physical Impact

Can physical impact as a result of a cylinder being dropped or in a motor vehicle accident initiate a decomposition reaction?

It is not uncommon for a motor vehicle accident to spill many cylinders onto the roadway such as the incident below with a plumber's van

Extensive Testing by BAM using explosives attached to the cylinder sidewall has concluded that there is not enough energy introduced during physical impact to initiate the decomposition reaction.
In the 2 MATS trailer rollovers (2007 TX and 2008 LA) reviewed by the NSTB hundreds of cylinders were propelled out of the trailer, impacting the roadway. Half had their valves sheared and the released gas ignited. These were ignited likely due to sparks generated when the metal cylinder struck the ground or by static from the escaping gas. The flames impinged on other nearby cylinders causing the PRDs to melt to also vent. No cylinder ruptured due to a decomposition reaction in either incident.

After a fire

Acetylene cylinders can be exposed to excessive temperatures during a fire as radiant heat and/or direct flame impingement. In a fully engulfing fire, the PRDs will melt and vent the contents, while direct flame impingement onto the sidewall of the cylinder may not melt the PRDs. This could initiate the decomposition reaction by softening the metal at that location and increasing the internal cylinder pressure. This could cause the cylinder wall to bulge out slightly from the porous mass creating a void where the decomposition reaction can continue after the fire is extinguished. A temperature > 662^{o}F (350^{o}C) will initiate the decomposition reaction.

Visually assess the cylinder exterior. Is there bubbled paint (>500^{o}F) or charred paint(750^{o}F)? Any bulging of the cylinder? If you wet the cylinder in that area does it steam or immediately dry? All these are signs of a decomposition reaction within the cylinder that might be continuing. Immediately examine the cylinder with a thermal imaging camera and cool using a hose stream for an hour if any hot spots are found. As a best practice the cylinder is then put into a drum of water overnight. If the cylinder shows a uniform temperature and there are no hot spots there is no reaction going on within the cylinder.

During a fire if the PRDs melt the acetylene will have all vented, only acetone or DMF will remain in the cylinder. If the fire burned long enough the acetone or DMF will also have vaporized.

If they are nested tightly together on a pallet and there was a fire around it, first thermally image the cylinders on the perimeter because that's where it is more likely for radiant heat and/or flame impingement onto the cylinder walls. Then put a hose stream on them in place for an hour assuming that there might be an initiation point that cannot be seen between the cylinders. After an hour remove cylinders from the pallet and thermally image all around them for hot spots. While it is unlikely it is a safety practice to ensure no cylinder has a "hot" spot. If one is found water spray for an hour and recheck.

Even if the PRD is activated and flames are shooting out of the cylinder, the fire can create sufficient heat to cause an adjacent cylinder that is also venting to explode. The following pictures are from the 2007 Dallas MATS incident. All the cylinder PRDs on the cylinder collar have melted and are venting

flaming acetylene. The site manager tried to control the incident using a hose stream and was unsuccessful (see red circle).

Multiple cylinders exploded severely injuring these 2 employees. This spread to many other cylinders and trailers on site, burning for 9 hours.

Flooding quantities of water is required to cool all of the cylinders on the trailer. Only a properly designed deluge system will be effective in controlling this type of incident. This has been required under NFPA 55 since 2012.

While rupture of an acetylene cylinder is extremely unlikely after the fire is extinguished, the emergency responder must assume that this can be the case for most incidents involving acetylene cylinders in a fire.

Eugene Ngai