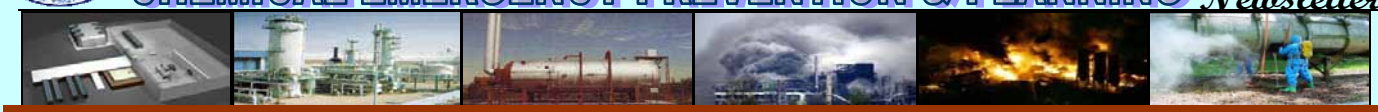
Clean Air Act 112(r) Risk Management Program (RMP) EPCRA

CHEMICAL EMERGENCY PREVENTION & PLANNING Newsletter



December 2006- January 2007 US EPA Region 10

Inside This Issue

Reporting Exemption for Certain Air Releases of NOX (NO and NO2)

EPA issued a final rule that addresses the frequency and level of reporting associated with releases of nitrogen oxide (NO) and nitrogen dioxide (NO2) under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Emergency Planning and Community Right to Know Act (EPCRA). This final rule is effective November 3, 2006.

In this rule, EPA broadens the existing reporting exemptions for releases that are the result of combustion of less than 1,000 pounds of nitrogen oxide and less than 1,000 pounds of nitrogen dioxide to the air in 24 hours. These may also include emissions from detonation or processes that include both combustion and non-combustion operations, such as nitric acid production. This administrative reporting exemption is protective of human health and the environment and consistent with the Agency's goal to reduce unnecessary reports given that the levels for which the Clean Air Act regulates nitrogen oxides are considerably higher than 10 pounds. In addition, the Agency believes that the information gained through submission of the reports for those exempted releases would not contribute significantly to the data that are already available through the permitting process to the government and the public.

To determine whether your facility is regulated by this action, you should carefully examine the criteria in section I.C of this final rule preamble and the applicability criteria in § 302.6 of title 40 of the Code of Federal Regulations. The rule may be found at http://yosemite.epa.gov/oswer/ceppoweb.nsf/content/epcra_law.htm#FRNotices. For further information contact: Lynn Beasley, Regulation and Policy Development Division, Office of Emergency Management, OSWER (5104A), EPA, 1200 Pennsylvania Ave., NW., Washington, DC 20460; telephone number: (202) 564–1965; fax number: (202) 564–2625; e-mail address: beasley.lynn@epa.gov.

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Modification of Threshold Planning Quantity for Isophorone Diisocyanate

EPA issued a direct final rulemaking and also a proposed rulemaking to adjust the reportable quantity (RQ) for Isophorone Diisocyanate (IPDI) from 100 pounds to 500 pounds. Entities that may be affected by this action are those facilities subject to 40 CFR part 355, Emergency Planning and Release Notification. This rule is effective October 8, 2003.

Reportable quantities for many Extremely Hazardous Substances (EHS) under the Emergency Planning and Community Right to Know Act (EPCRA) were adjusted to their threshold planning quantities (TPQ) in a final rule on May 7, 1996. On September 8, 2003 EPA modified the TPQ for IDPI to 500 pounds; however, EPA inadvertently omitted an RQ adjustment for this substance. Therefore, EPA is now adjusting the RQ for IPDI to be 500 pounds. This revision is being made without prior proposal because the Agency views the revision as non-controversial. The rulemaking may be found at http://yosemite.epa.gov/oswer/ceppoweb.nsf/content/epcra_law.htm#FRNotices.

For questions on the contents of this document, contact: Sicy Jacob, CEPPO (5104A), EPA, 1200 Pennsylvania Avenue, NW., Washington DC 20460, Telephone: 202 -564-8019; Fax: 202-564-8233; email: jacob.sicy@epa.gov.

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FEATURE: GAS CYLINDER SAFETY GUIDELINES

Compressed Gas Cylinder Storage and Handling

Compressed gas cylinders are used in many workplaces to store gases that vary from extremely flammable (acetylene) to extremely inert (helium). Compressed gases present several hazards. Labels on the cylinder and the Material Safety Data Sheet (MSDS) supplied with the gas tell you about the hazardous properties of the gas; such as toxic, flammable, or oxidizer. In addition to the gas chemical hazards, compressed gas cylinders pose other hazards simply because they contain gas under pressure.

Many compressed gas cylinders are stored at extremely high pressures (up to 2,500 psig). Mishandled or improperly stored cylinders may rupture violently. A sudden release of these gases can cause a cylinder to become a dangerous missile-like projectile. Cylinders have been known to penetrate concrete-block walls.

If a neck of a pressurized cylinder should be accidentally broken off, the energy released would be sufficient to propel the cylinder to over three-quarters of a mile in height. A standard 250 cubic foot cylinder pressurized to 2,500 PSIG can become a rocket attaining a speed of over 30 miles per hour in a fraction of a second after venting from the broken cylinder connection.

If handled and stored properly, compressed gas cylinders are safe. If handled or stored improperly, the same cylinders can present a severe hazard to people and the surrounding area.

What should you do when you receive cylinders?

Inspect all incoming cylinders before storing to ensure they are undamaged and properly labeled (cylinders must comply with NFPA and DOT labeling and OSHA hazard communication requirements). Do not accept delivery of defective or unidentified cylinders. Be sure they are not giving off odors, visible fumes or hissing sounds. Check that the cylinder was last tested within the required time (usually five years).

Also check that the cylinder labels are intact and that they match other identifying markings on the cylinder. Do not rely on cylinder color to identify the gas. Different suppliers may use different colors for cylinders of the same gas. In addition, colors appear different under artificial lights and some people are color blind.

Call compressed gases by the name on the supplier label. This reduces confusion, promotes recognition of the hazards involved and precautions to take, and can prevent accidental use of the wrong gas. If oxygen is called "air," someone who wants air to run a tool may use oxygen with possible serious results. Leave the valve cap securely in place until the cylinder is to be used. Inspect the cylinder valve by looking through the ports in the valve cap. Do not accept rusted or otherwise damaged valves and fixtures.

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Compressed Gas Cylinders
Authority and References:

OSHA 29 CFR 1910.101 (Compressed Gases - General Requirements)
OSHA 29 CFR 1910.102 (acetylene)
OSHA 29 CFR 1910.103 (hydrogen)
Compressed Gas Association (CGA) (safety publications)
National Fire Protection Agency (NFPA) (compressed gas)

How do you store compressed gas cylinders?

Compressed gas cylinders are the most common source of gas for many operations. Due to their hazardous nature, safe storage and handling of compressed gas cylinders are required by the following regulations:

- The Compressed Gas Association (**CGA**) – has many publications designed to ensure the safe handling of compressed gases.
- **OSHA** (29 CFR 1910.101, Compressed Gases) - has regulations governing the use of compressed gases, with the CGA pamphlets incorporated by reference.
- The National Fire Protection Agency (**NFPA**) - has standard requirements for the storage, use and handling of portable gas cylinders.

The general safety guidelines below from CGA and NFPA will minimize hazards when storing and handling compressed gas cylinders. They are intended as general guidance only, and not a substitute for any applicable federal, state or local regulations.

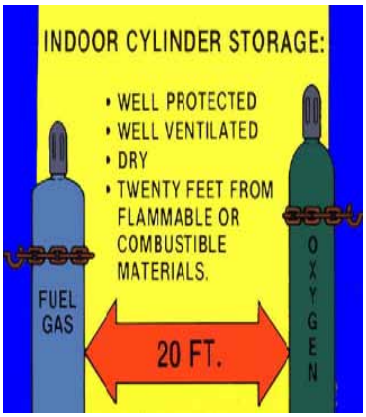
- Signs should be conspicuously posted in areas where toxic or flammable compressed gases are stored, identifying the substances and appropriate precautions (e.g., HYDROGEN - FLAMMABLE GAS - NO SMOKING - NO OPEN FLAMES). (CGA; NFPA)

- Compressed gas cylinders must be firmly secured at all times to prevent cylinders from tipping or falling. An appropriate clamp, belt or chain should be used for this purpose. (CGA; NFPA)
- Liquefied flammable gas cylinders should be stored in an upright position, or such that the pressure relief valve is allowed to remain in the gas phase. Cylinders loaded with liquefied gas are not completely filled; a small vapor space is left to allow for expansion if the cylinder is heated. (CGA; NFPA)

- Only Compressed Gas Association (CGA) standard combinations of valve and fittings should be used on compressed gas systems. This reduces the possibility of accidentally mixing incompatible gases due to an interchange of connections. (CGA)
- Compressed gas cylinders should only be handled, used or stored in locations where they are well-ventilated, not exposed to heat or direct sunlight, pressures, corrosive substances or dampness. Do not use a cylinder as an electrical ground connection. (CGA; NFPA)
- All fuel or flammable gases (examples: acetylene, propane, hydrogen) must be stored away from oxidizing gases (examples: fluorine, nitrogen oxide), toxic gases and oxygen cylinders at a minimum of 20 feet or separated with an approved fire wall. (CGA; NFPA)
- Cylinders should never be used as rollers for moving materials, for supporting other items, or for other unintended purposes. (CGA)
- Flammable gas cylinders whether full or empty must not be located near an exit or any location which could block an exit. (NFPA)

What is Wrong? What is Right?

Upright and Secured ?



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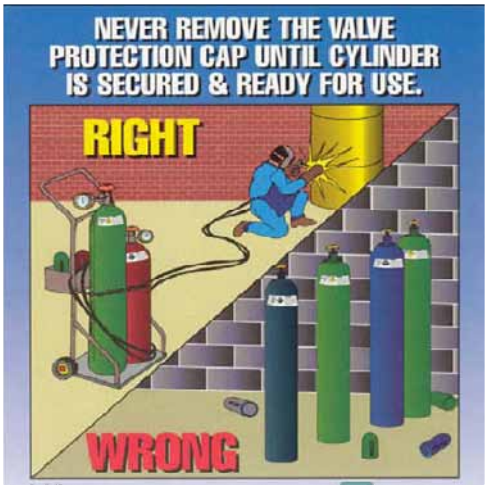
Compatible ?



ACETYLENE CYLINDER SAFETY PRACTICES

- Never use a leaking cylinder.
- Always store acetylene and oxygen separately.
- Always store acetylene cylinders vertically. Acetylene cylinders are packed with porous rock that is saturated with acetone.
- Use a leak detection fluid to check fittings and connections for leaks.
- Never attempt to store or inject acetylene gas into any type of vessel, tank, or enclosure.
- Acetylene gas regulators should not exceed a setting of 15 psig.
- Flame arrestors and check valves should be installed at both the torch base hose connections and at the regulator hose connections.
- Close the cylinder valve before shutting off the regulator to bleed gas from the regulator.
- If cylinders are not used for a period of time, remove the gauges and regulators and cap the cylinders.

(Source: DOE)

- Employees storing, using and handling compressed gases should understand the properties, hazards and safety precautions by consulting their supervisors, Material Safety Data Sheets or other references. (CGA)
- The cylinder valve cap must be secured on the head of a cylinder whenever it is not in use. This protects the vulnerable cylinder valve and prevents the cylinder from becoming a dangerous projectile in case of an accident. Do not use valve caps to lift cylinders. (CGA; NFPA)

- Inspect storage areas regularly for any deficiencies such as damaged or leaking cylinders and poor housekeeping. Correct all deficiencies as soon as possible. (CGA)
- Segregate empty cylinders from full cylinders. When empty cylinders are to be returned to the vendor, mark them "Empty" or "MT." Keep valves closed on empty cylinders. (CGA)

- The quantities of compressed gas cylinders should be kept to the minimum needed for an operation. (CGA)
- Transport cylinders on specially built hand carts or trolleys or other devices designed for this. All transport devices should have some way of securing cylinders to prevent them from falling. (CGA)

What should you do in an emergency?

An emergency response plan is to be prepared and updated whenever compressed gases are produced, handled, stored or used (NFPA-55). The MSDSs for the gases are a starting point for drawing up an emergency plan. MSDSs have specific sections on spill and leak procedures, first aid instructions, and fire and explosion hazards. If the directions in each MSDS section are not clear or seem incomplete, contact the gas supplier or manufacturer for help.

Many other sources can also help develop emergency plans. Local fire departments can assist with fire emergency plans and training. Occupational health and safety and environmental enforcement agencies, safety associations, and private consultants can supply useful information.

Act fast in emergencies such as chemical fires or gas cylinder leaks.

- Evacuate the area at once if you are not trained to handle the problem or if it is clearly beyond your control.
- Alert other people in the area to the emergency.
- Call 911 and the fire department immediately.
- Report the problem to the people responsible for handling emergencies where you work.
- Obtain first aid and remove all contaminated clothes if you have been exposed to harmful chemicals.
- Only specially trained and properly equipped people should handle emergencies. Nobody else should go near the area until it is safe.

(References: CGA; NFPA; DOE; Harvard-Smithsonian)

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Safety Bulletin

Manufacture, Marking, and Sale of Untested Compressed Gas Cylinders

The Pipeline and Hazardous Materials Safety Administration (PHMSA) was recently notified of the manufacture, marking, and sale of certain high pressure DOT exemption cylinders that were not tested in accordance with applicable regulatory requirements.

These cylinders were manufactured and/or distributed by Luxfer, Inc. (Luxfer), Riverside, CA. Luxfer and its independent inspection agency, Arrowhead Industrial Services, Inc. (Arrowhead), reported to PHMSA that 6,325 high pressure cylinders manufactured to the DOT CFFC and FRP-1 standards as authorized in DOT- E 10915, DOT E 9634, and DOT-E 9894, had been shipped from Luxfer without undergoing the required autofrettage and hydrostatic tests.

In a joint effort, Luxfer and Arrowhead have retrieved 2,581 of the untested cylinders. The model numbers and serial numbers of the remaining 3,744 cylinders may be found in pages 25634 through 25639 of the Federal Register, available at: http://hazmat.dot.gov/regs/notices/sa/71fr 25633.pdf

Only cylinders with the listed model numbers and serial numbers are affected. A person with a listed cylinder should discontinue use of the cylinder and return it to Arrowhead so that the autofrettage and hydrostatic test can be completed before its next use.

For more information, please contact the Pipeline and Hazardous Materials Safety Administration, Mr. Wayne Chaney, (202) 366-4700.
(Source: DOT, May 2006)

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Propane Cylinders and Anhydrous Ammonia

It has come to the attention of the National Propane Gas Association that propane cylinders are being used in the manufacturing of Methamphetamines. This drug is commonly referred to as 'crank'. Manufacturers of this illegal substance are using propane cylinders for the storage and the use of anhydrous ammonia. These cylinders have been found in many states at cylinder exchange and refilling locations as well as in hotel rooms and mobile laboratories, where the manufacturing of this illegal substance takes place.

As observed in the illustrations, a blue-green stain on any brass portion of a service valve is evidence that it may have been in contact with anhydrous ammonia. The pungent odor of ammonia on or near the cylinder is also an indication. If you suspect that a propane cylinder contains or has contained anhydrous ammonia, exercise extreme caution and restrict access to the area.

It can be dangerous to move the cylinder due to the unknown integrity of the cylinder's service valve. If you determine that it must be moved, keep in mind that hazards due to valve expulsion can be reduced by pointing the end of the container in which the valve is placed away from yourself and others and towards the safest direction.

Immediately contact your Fire Department, Hazardous Materials Emergency Response Unit or the nearest office of the United States Department of Justice's Drug Enforcement Administration (DEA) for information on properly disposing of the cylinder.

Caution!

The brass valve in a propane cylinder will be damaged if it comes in contact with anhydrous ammonia. This deterioration will lead to cracking of the valve body or its components and can ultimately result in a violent, unexpected expulsion of the valve from the cylinder (causing the release of the hazardous contents or the cylinder becoming a dangerous projectile).
(Source: The National Propane Gas Association)

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Inspection Required for Chlorine Cylinder Valves

Although they are not common, there have been reports of both cylinder and ton container valves being found with cracks. Cracked cylinder valves have been reported in the chlorine industry from time to time over the years since 1927. There are two reported incidents in the U.S. and Canada where an actual leak of chlorine is known to have occurred. Fortunately, most cracks have been discovered before any leaks happened.

The cracks have been found running longitudinally through the threads by the packing nut. (Note: this is the nut that the valve stem goes through, see photo.) The crack may vary from fractions of a millimeter up to 30 millimeters in length. In some instances, a second crack appears perpendicular to this crack about 10 to 30 millimeters below the bottom packing thread. One such crack covered a distance of about 120 degrees around the valve body.

What can you do ?

1. Valves should be inspected each time before they are opened or reopened. It appears that the valves will not leak until they are opened since the valve will be sealed at the stem. If a crack is identified in the field, the valve should be shut off, tagged and isolated, and the supplier contacted at once for disposition. Do not open the valve!

2. If no cracks are found, you can connect your system to the container valve and by following the supplier recommended procedures, open the valve. A careful check using only the vapors from a 20 degree baume ammonia water (ammonium hydroxide solution) will produce a visible white gas if there is a leak. If a leak is found, close the valve and contact your chlorine supplier immediately.

3. If you are using ton container valves on manifolds or in chlorine headers, you should inspect these as well every time you change chlorine containers. If a crack is found, close the valve and contact your equipment supplier immediately for instructions.

(**Note**: The Chlorine Institute, Inc. is currently evaluating new information raised concerning the use of ammonia vapors to test for chlorine leaks on valves and fittings made of copper or brass alloys. There was indication that ammonia may cause problems with such metal alloys. The Chlorine Institute urges anyone testing for chlorine leaks with ammonia water on brass or copper alloys to take care that only the ammonia vapor and not the liquid solution comes into contact with the alloy).
(Condensed from: Chlorine Institute, Inc.)

Lessons Learned

Violent Failures of Older Compressed Gas Cylinders

Two recent explosions involved the violent failure of cylinders containing liquefied compressed gases. These incidents are vivid reminders that workers need to be aware of compressed gas cylinder shelf life limits.

In July 2005, a cylinder of anhydrous hydrogen fluoride (HF) failed explosively in an unoccupied UC Santa Barbara lab (see photos), causing considerable damage. It now appears that moisture entered the cylinder and promoted corrosion. The fluorine in the HF reacted with the iron in the cylinder wall, promoted by moisture, to form iron (ferric) fluoride. HF in a cylinder is mainly a liquid with a very low vapor pressure, between only 5 to 15-pounds per square inch gauge (psig). The corrosion process formed hydrogen, a true gas, and the pressure inside the cylinder increased as more and more hydrogen was formed by corrosion. In addition, the chemical reaction with the metal in the cylinder weakened the cylinder until the cylinder failed. The customary shelf life for HF cylinders is one or two years, depending on the vendor. The cylinder that exploded was at least seven years old.

In April 2005, a cylinder containing a residual amount of hydrogen cyanide (HCN) burst in a US Army lab at Edgewood, Maryland. HCN in a cylinder is also a liquid with the gas in the space above it. Like HF, the vapor pressure of HCN is very low, essentially 0 psig at room temperature and about 10 psig at 100°F. With the presence of heat, over time the HCN forms a polymer with itself. A tap on the cylinder could cause a flake of polymer from above the pool of liquid to fall onto the film of polymer. This will cause the remaining pooled liquid to polymerize extremely rapidly, producing hot gas that will cause the cylinder to fail explosively. Older cylinders can be extremely shock sensitive so they need to be removed by specially trained hazardous materials crews. The Army's laboratory activities at Edgewood were disrupted for months while other cylinders of HCN were removed. For this reason the customary storage lifetime for cylinders of hydrogen cyanide is just six months.

Recommended Actions

1. Ensure that all vendor-filled cylinders have a label or properly identified to avoid costly disposal issues.

2. Return HF and HCN cylinders nearing the ends of their shelf lives to the vendor.

3. Keep moisture out of HF cylinders to minimize hydrogen buildup. This can be done by placing a suitable moisture trap between the gas outlet or apparatus the cylinder is connected to and the cylinder.
   Note: Also keep moisture out of hydrogen chloride and hydrogen bromide cylinders to avoid leaks caused by corrosion.

4. If you order HCN, or if HCN is an ingredient in gas mixtures, check with the manufacturer for the cylinder's shelf life. The shelf life for cylinders of pure HCN will typically be just six months.

(Source: DOE- LLNL)

The remains of the HF cylinder

Laboratory equipment damaged by the exploding HF cylinder.

"Lessons Learned are to be shared in order to improve operational safety by benefiting from the experience of others. Lessons Learned are to be prepared and distributed whenever there is an opportunity to share a valuable new work practice or warn others of an adverse practice, experience, or product. "

- DOE, LLNL Integrated Safety Management System

Dangers of Gas Cylinders in High Temperatures

June 24, 2005 was a hot, sunny summer day in St. Louis, with temperatures reaching 97F. Operations at a gas cylinder packaging and distribution facility 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 and activated the fire alarm. Propylene gas had been released from the relief device on a cylinder valve and ignited. Workers and customers evacuated. The fire spread to adjacent propane and acetylene cylinders, which ignited and began exploding, flying into other areas of the facility, and spreading the fire. After 4 minutes, the fire covered most of the facility's flammable gas cylinder area and explosions were frequent.

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 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 were found as far as 800 feet away.

Facility Damage

Community Damage

Did You Know?

- Some materials stored in containers such as drums, cylinders, and pails can be heated to a hazardous temperature if they are stored outdoors and exposed to direct sunlight.
- The hazard can be a result of decomposition, polymerization, or other chemical reaction, or it can simply be over pressurization of the container because of the vapor pressure of the contents, as in the incident described above.
- In this incident, direct sunlight, and an unusually hot day, probably raised the temperature of the cylinder and its contents to about 150F, sufficient to open the relief device and release the gas.

What Can You Do?

- Follow guidelines for safe storage of chemical containers found in the material data sheet (MSDS).
- For gas cylinders, follow guidelines from industry associations such as the Compressed Gas Association (CGA), consensus standards such as those from the National Fire Protection Association (NFPA), and recommendations from material suppliers.
- Minimize the number of cylinders in process areas.
- Read the Chemical Safety Board (CSB) Bulletin on this incident and recommendations for prevention of similar incidents at website: http://www.csb.gov/safety_publications/docs/CSBPraxairSafetyBulletin.pdf

The Sleeping Giant

Many of us are surrounded by compressed gas cylinders. Here is a reminder of just what respect they command.

GET TO KNOW ME

I can contain very high pressure.
I wear a label to identify the gas I am holding.
My color does not tell you what gas I contain.
I am only one piece of a two-part system. Without a correct regulator or manifold I cannot function safely.

KNOW HOW TO USE ME

Know how to safely install and remove me from your system.
Make sure I am properly secured when in use and when stored.
Open my valve slowly when I am to be used.
Close my valve when you are done.
Know the dangers of my contents, read the MSDS, and follow proper procedures when using me.

WHEN THINGS GO WRONG

If my valve or regulator snaps off, all my power is unleashed through an opening no larger than a pencil.

I will jet away faster than any dragster.
I will smash through brick walls.
I will spin, ricochet, crash and splash through anything in my path.

TO BE MY MASTER REMEMBER

Secure me,
Cap me, and
Always follow recommended safety procedures.