United States
Environmental Protection
Agency

Research and Development

Air and Energy Engineering
Research Laboratory
Research Triangle Park NC 27711

EPA/600/S8-87/034n Sept. 1989

EPA

Project Summary

Prevention Reference Manual: Chemical Specific, Volume 14: Control of Accidental Releases of Phosgene

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Interest in reducing the probability and consequences of accidental toxic chemical releases that might harm workers within a process facility or people in the surrounding community has prompted preparation of this manual and a series of companion manuals on the control of accidental releases of toxic chemicals. This manual, on phosgene, is one of several chemical-specific Prevention Reference Manuals.

Phosgene is a highly reactive and corrosive liquid that has an IDLH (Immediately Dangerous to Life and Health) concentration of 2 ppm, making it an acutely toxic hazard.

To reduce the risk of an accidental release of phosgene, the potential causes of releases in facilities handling phosgene must be identified. The phosgene manual provides examples of such causes, as well as of measures that may be taken to reduce the accidental release risk. Such measures include recommendations on plant design practices; prevention, protection, and mitigation technologies; and operation and maintenance practices. Cost estimates of prevention, protection, and mitigation measures are provided.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Increasing concern about the potentially disastrous consequences of accidental releases of toxic chemicals has prompted preparation of a series of manuals for regulators and industry personnel on the prevention of accidental releases of toxic chemicals. The manual on phosgene is one of several chemical-specific manuals that address issues associated with the storage, handling, and process operations involving toxic chemicals as they are used in the U.S.

In the U.S. and abroad, few significant releases of phosgene have occurred; however, in Hamburg, Germany, in 1928 a phosgene storage tank failed, killing 10 people, and in LaPorte, Texas, in 1969 an accidental phosgene release at a chemical plant injured 2 people.

Phosgene is manufactured commercially by reacting carbon monoxide with chlorine over a carbon catalyst. Most of the phosgene produced is used captively at the production facility, although it is also shipped in 150-lb (68kg) and 1-ton (907 kg) cylinders. In the U.S., 85% of the phosgene produced is used in the manufacture of isocyanates, which are precursors of polyurethane foam and rubber. Phosgene is also used in the production of polycarbonates and specialty chemicals such as herbicides, pesticides, dyes, and pharmaceuticals.

Potential Causes of Releases

Phosgene releases can originate from many sources, including ruptures in process equipment, separated flanges, actuated relief valves or rupture discs, and failed pumps or compressors. Phosgene is not explosive or flammable; however, it is highly reactive and highly toxic when inhaled. When inhaled, phosgene slowly hydrolyzes to hydrochloric acid in the respiratory system.

The reactivity of phosgene makes it corrosive. Evaporators and metering and control equipment are especially sensitive if they are in intermittent use where moisture might enter the system. Either liquid or vapor phosgene releases can occur. Failures leading to accidental releases of phosgene can be due to process, equipment, or operational causes.

Possible process causes of phosgene releases include:

- Overpressure of any storage or process vessel containing phosgene, caused by decomposition of phosgene to hydrogen chloride and carbon dioxide from contamination with water;
- Overpressure of storage or process vessels containing phosgene caused by contamination of other phosgene reactive materials;
- Excess phosgene feed leading to overfilling or overpressuring of equipment;
- Loss of agitation in batch reactor systems;
- Loss of cooling or temperature control of reactor systems resulting in thermal decomposition; and
- Loss of pH control in caustic slurry reactors resulting in the decomposition of phosgene to carbon dioxide and hydrochloric acid, which could result in overpressure and an accidental release.

Equipment-caused accidental releases result from hardware failure (e.g., excessive stress due to improper fabrication, construction, or installation); weakening of equipment from excessive stress, external loading, or corrosion; mechanical fatigue and shock; creep failure in equipment subjected to extreme operational upsets, especially excess temperature; stress corrosion cracking; and all forms of corrosion.

Operation-caused accidental releases result from incorrect operating and maintenance procedures or human errors such as: overfilled storage vessels; errors in loading and unloading procedures; inadequate maintenance; lack of inspection and non-destructive testing of vessels and piping to detect corrosion weakening; and incomplete knowledge of the properties of a specific chemical or of the process or chemical system.

Hazard Prevention and Control

The prevention of accidental releases depends on a combination of technological, administrative, and operational practices that apply to the design, construction, and operation of facilities where phosgene is stored and used. Important areas to be considered are process design, physical plant design, operating and maintenance practices, and protective systems.

The primary focus of process design is on how the process is controlled in terms of the basic process chemistry and the variables of flow, pressure, temperature, composition, and level. The process design must be evaluated to see how deviations from expected design conditions might start a series of events that could result in an accidental release. A review of the variables of process design might lead to suggested modifications that would enhance the integrity of the process, such as changes in quantities of materials used, process pressure and temperature conditions, unit operations used, the sequence of operations, process control strategies, and the instrumentation used.

Physical plant design involves plant equipment, siting and layout, and transfer/transport facilities. The most important considerations in selecting equipment construction materials for phosgene service are the temperature and moisture content of the phosgene. Temperature is important because phosgene decomposes to carbon monoxide and chlorine at high temperatures, and most metals will ignite at a given temperature in the presence of chlorine. Moisture content is important because moist or wet phosgene hydrolyzes to hydrochloric acid, which is very corrosive. Dry phosgene is not considered corrosive.

Because of the large inventories contained in phosgene storage vessels, they are one of the most hazardous parts of a phosgene system. A variety of safety features are usually incorporated into phosgene storage vessels. Overpressure protection devices are routinely routed to a containment vessel or to a caustic scrubber. With liquid phosgene, overfilling and overheating are important because of the liquid's high coefficient of thermal expansion. Since there is no way to contain a phosgene discharge from vessels used to transport phosgene (150- and 2000-lb cylinders), great care mus be taken in transporting and storing thes vessels; exposure to temperatures abov 125°F (52°C) must be avoided.

Overfilling can be prevented by usin level sensing devices, pressure relief de vices, and adequately trained personne Selection of such devices must take int account the corrosiveness of phosgene especially in contact with moisture. Con tainers should be valved to allow th vessel to be isolated from the process t which the phosgene is being fed.

The design of piping systems shoul be simple, minimizing the number c joints and connections. Pipes should b sloped, and drainage should be provide at low points. When applicable, an expan sion chamber should be installed t prevent a rupture caused by thermal e pansion.

The siting of facilities and individu equipment should minimize personne exposure during a release. Ready ingres and egress should be available in a emergency. Large inventories of phos gene should be kept away from potenti sources of fire or explosion. Phosgen piping should not be located adjacent t other piping under high pressure c temperature. Storage facilities should b segregated from the main process an from control rooms, offices, utilities, sto age, and laboratory areas.

Protection technologies for phosgene or those measures taken to capture c destroy the chemical if it has breache primary containment, include enclosure scrubbers, incinerators, and flares. Enclo sures can capture phosgene spilled c vented from storage or process equi ment, thereby preventing immediate di charge of the chemical to the enviro ment. Although specially designed encl sures for phosgene service have n been widely used, such containme structures equipped with monitorir equipment and alarms might be approp ate. The enclosures should be gastig and have a ventilation system designe to draw in air when the building is vente to a scrubber. The bottom section such a building should be liquidtight retain spilled liquid phosgene.

Scrubbers are a traditional way to a sorb toxic gases from process stream Types of scrubbers that might be appr priate for phosgene include spray towe packed bed scrubbers, and venturis.

Incinerators can be used to contr phosgene releases from vents and pre sure relief discharges, from proce equipment, and from secondary co tainment structures. Phosgene discharges could be mixed with fuel and air in a thermal oxidation unit to convert the toxic vapor to carbon monoxide and chlorine since phosgene decomposes to these gases at 1,472°F (800°C). The system must be constructed of corrosion-resistant materials. Also, an acid-gas scrubber would be needed to remove the hydrogen chloride and chlorine from the vent gases.

Flares must be so designed that a large phosgene release would not overwhelm them and lead to a flame blowout or to a temperature insufficient to completely destroy the phosgene. An acid-gas scrubber would also be required for this system.

If a large release of phosgene occurs, workers must be rescued from the immediate vicinity of the accident and people downwind of the release must be evacuated. The effects of the released chemical on the plant and community must be mitigated by such measures as physical barriers, water sprays and fogs, and foams, where applicable. Such mitigation measures divert, limit, or disperse the chemical that has been spilled or released to the atmosphere.

The foregoing techniques for preventing, containing, or mitigating an accidental release of phosgene must also be supported by management safety policy, training, and proper operating and maintenance procedures.

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The complete report, entitled "Prevention Reference Manual: Chemical Specific, Volume 14: Control of Accidental Releases of Phosgene," (Order No. PB 89-155 048/AS; Cost: $21.95, subject to change) will be available only from:

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