United States
Environmental Protection
Agency

Air and Energy Engineering
Research Laboratory
Research Triangle Park NC 27711

Research and Development

EPA/600/S8-87/034g Feb. 1988

EPA

Project Summary

Prevention Reference Manual: Chemical Specific, Volume 7: Control of Accidental Releases of Chloropicrin (SCAQMD)

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The South Coast Air Quality Management District (SCAQMD) of California has been considering a strategy for reducing the risk of a major accidental air release of toxic chemicals. The strategy, which will serve as a guide to industry and communities, includes monitoring activities associated with the storage, handling, and use of certain chemicals. This manual summarizes technical information that will assist in identifying and controlling chloropicrin-associated release hazards specific to the SCAQMD.

Chloropicrin has an immediately dangerous to life and health (IDLH) concentration of 1 ppm, making it a substantial acute toxic hazard. Potential causes of accidental releases from processes that use chloropicrin in the SCAQMD are identified, as are specific measures that may be taken to reduce the risk of accidental release. Such measures include recommendations on: plant design practices; prevention, protection, and mitigation technologies; and operation and maintenance practices. Conceptual costs of these measures are estimated.

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

The South Coast Air Quality Management District (SCAQMD) conducted a study in 1985 to determine the presence, quantities, and uses of hazardous chemicals in the SCAQMD, which comprises Los Angeles, Orange, San Bernandino, and Riverside Counties. The study resulted in a 1985 report, "South Coast Air Basin Accidental Toxic Air Emissions Study," which outlined an overall strategy for reducing the potential for a major toxic chemical release.

The strategy involves monitoring industry activities associated with the storage, handling, and use of certain chemicals to minimize the potential for accidental chemical releases or the consequences of any releases that might occur.

This volume of the manual discusses storage and handling practices and process operations relating to the prevention of accidental releases of chloropicrin as it is used in the SCAQMD. Chloropicrin (CCl_3NO_2) is manufactured commercially from bleaching powder and picric acid or by the chlorination of nitromethane in the presence of caustic. It is used primarily as an insecticide, a soil fumigant, and a warning agent in chemical fumigants. In the SCAQMD, chloropicrin is manufactured from nitromethane and sodium hypochlorite and is used in the formulation of chloropicrin-methyl bromide.

Potential Causes of Releases

Chloropicrin releases can originate from many sources, including leaks or ruptures in vessels, piping, valves, instrumentation connections, and process machinery such as pumps. The primary hazard associated with the manufacture of chloropicrin is the possibility of a runaway reaction

caused by the exothermic nature of the chlorination reaction. Adequate temperature control and agitation are required to prevent a hazardous release of toxic material.

Chloropicrin decomposes violently when heated above its normal boiling point, 112°C, to severely toxic gases, including nitric oxide, phosgene, nitrosyl chloride, chlorine, and carbon monoxide. Most metals are corroded or tarnished to some degree by chloropicrin, which is also incompatible with strong oxidizers.

Possible process causes of a chloropicrin release include: (1) excess nitromethane feed to a batch reactor, leading to excessive exothermic reactions; (2) excess feeds in any part of the system, leading to overfilling or overpressuring equipment; and (3) overpressure in chloropicrin storage vessels.

Possible equipment causes of accidental releases resulting from hardware failures include excessive stress caused by improper fabrication, construction, or installation; or failure of vessels, pipes, or pumps because of corrosion, external loadings, or excessive stress.

Operational causes of accidental releases resulting from incorrect operating and maintenance procedures and operator error include overfilled storage vessels, errors in transfer procedures, inadequate maintenance, improper system operation, and lack of inspection and nondestructive testing of vessels and piping to detect corrosion weakening.

Hazard Prevention and Control

Prevention of accidental releases requires careful consideration of the design, construction, operation, and protective systems of facilities where chloropicrin is manufactured, stored, and used.

The primary consideration in the manufacture of chloropicrin is the prevention of overheating resulting in boiling of the batch reactor contents that might lead to overpressure. Equipment failure is also possible if corrosion has weakened process equipment. Most metals are corroded or tarnished by chloropicrin, but not enough to prevent their use as construction materials. Metals also tend to have a catalytic effect on the decomposition of chloropicrin. Equipment used in chloropicrin service is commonly lined with tetrafluoropolyethylene, vinylidene chloride, or polyvinylidene fluoride to prevent corrosiion. Aluminum, magnesium, and their alloys should not be used in chloropicrin service since it reacts violently with these materials.

Release prevention for vessels includes overpressure protection, temperature control, and corrosion prevention. Process vessels are usually protected by pressure relief valves and/or rupture discs. The correct design and use of pipe supports is essential to reduce overstess and vibration that could lead to piping failure. All piping should be situated away from fire and fire hazards since chloropicrin can explode violently above its boiling point. If possible, piping carrying chloropicrin should not be routed near other processes or piping networks that might present an external threat. Many of the concerns and considerations for chloropicrin piping also apply to valves and pumps.

Siting and layout of facilities and equipment should be designed to reduce personnel exposure in the event of a release. Large inventories of chloropicrin should be kept away from sources of fire or explosion hazard, and storage facilities should be segregated from the main process if possible.

Protection for the containment and neutralization of chloropicrin in the event of a release includes enclosures and scrubbers. Enclosures for chloropicrin releases could be concrete block or concrete sheet buildings or bunkers. The enclosure should be gastight and have a ventilation system designed to draw in air when the building is vented to a scrubber. Scrubbers appropriate for use with chloropicrin include spray towers, packed bed scrubbers, and venturis.

Mitigation technologies are those that reduce the consequences of a release if it occurs. They include physical barriers, water sprays and fogs, and foams. Such techniques divert, limit, or disperse the spilled or released chemical to reduce the atmospheric concentration and the area affected by the chemical. Secondary containment systems (e.g., impounding basins, dikes, and flotation devices and foams) can be used to reduce the evaporation rate of a spilled liquid.

Accidental releases of the materials can result from deficiencies of operation as well as of design. A sound maintenance program would include corrosion monitoring and relief valve testing. Employees should be trained in handling chloropicrin.

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The complete report, entitled "Prevention Reference Manual: Chemical Specific, Volume 7: Control of Accidental Releases of Chloropicrin (SCAQMD)," (Order No. PB 87-234 522/AS; Cost: $13.95, subject to change) will be available only from:

National Technical Information Service
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