United States
Environmental Protection
Agency

Research and Development

Air and Energy Engineering
Research Laboratory
Research Triangle Park NC 27711

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

EPA

Project Summary

Prevention Reference Manual: Chemical Specific, Volume 13: Control of Accidental Releases of Methyl Isocyanate

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Interest in reducing the probability and consequences of accidental toxic chemical releases that might harm workers within a process facility and 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. The manual on methyl isocyanate (MIC) is one of several chemical-specific prevention reference manuals. This manual summarizes information to help regulators and industry personnel identify and control release hazards associated with MIC.

To reduce the risk associated with an accidental release of MIC, the potential causes of accidental releases in process facilities that handle and store MIC must be identified. The MIC 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; prevention, protection, and mitigation technologies; and operation and maintenance practices.

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 resulted from the accident in Bhopal, India, in 1984, that killed approximately 2,300 people and injured 30,000 to 40,000 more. A toxic cloud of methyl isocyanate (MIC) was released from a storage tank at a Union Carbide of India pesticide plant. In another incident in New York in 1984, a pump failure at FMC Corporation led to the release of 45 gal. (170 L) of MIC. Nearby areas, including a school, had to be evacuated. Nine children and two adults were treated for eye irritation at a local hospital. Such accidents have increased interest in reducing the probability of accidental releases and prompted preparation of a series of manuals for regulators and industry personnel on the prevention of accidental releases of toxic chemicals. The manual on 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.

MIC is a small volume chemical. Total production in 1994 was estimated to be 30-35 x 10^6 lb (14-16 x 10^6 kg). Over 95% of MIC produced is used to manufacture pesticides and herbicides. Since the Bhopal release and tightening of transportation regulations, MIC is no longer shipped by rail car or in drums.

MIC, which is primarily made from the reaction of methylamine and phosgene is an intermediate in the manufacture of pesticides such as carbaryl (Sevin), aldicarb (Tenik), carbofuran (Furadan), and methamyl (Lannate).

Potential Causes of Releases

MIC is a highly volatile liquid at ambient conditions. It is a colorless liquid with a sharp odor at concentrations greater than 2 ppm. Liquid MIC is slightly less dense than water. Since the gaseous form is twice as dense as air, it tends to stay close to the ground if released in still air. It is highly flammable and reactive, particularly with compounds containing active hydrogen atoms. Since it is an unstable compound, extreme care should be taken to avoid conditions that could result in fires, explosions, and runaway reactions. MIC is usually stored and handled in dedicated stainless steel, nickel, and glass-lined equipment. Other materials could catalyze an undesirable reaction that might lead to overpressure releases. In some cases, the heat generated by a water/MIC reaction is sufficient to initiate self-polymerization. Tanks and reactors should not be filled to capacity to allow for possible expansion of the contents. Because MIC might react with water vapor in air, tank contents should be protected by a blanket of dry nitrogen. Also, MIC can react with itself in the presence of a catalyst to form trimethyl isocyanate. This reaction is also exothermic and could result in a violent runaway reaction.

The two basic causes of MIC releases are: uncontrolled chemical reactions, and spills and/or leaks that may occur during normal operation such as routine maintenance and cleaning of equipment. Uncontrolled chemical reactions of MIC, such as the one in Bhopal, are extremely dangerous. While the quantities of MIC likely to be spilled or leaked are not as great as those released because of an uncontrolled chemical reaction, the probability of spills and leaks occurring is much higher. Most of such MIC releases in the U.S. were the result of equipment failure. Failures leading to accidental MIC releases can be due to process, equipment, or operational problems.

Process causes are related to the fundamentals of process chemistry, control, and general operation. Possible process causes include:

- Contamination of MIC with rust from the nitrogen supply line, resulting in a runaway reaction;
- Contamination of MIC with a backflow of caustic solution from a scrubber, resulting in a runaway reaction;
- Contamination of MIC with brine used as a cooling fluid, resulting in a runaway reaction;
- Insufficient temperature and pressure monitoring equipment to detect process upsets or failure of instruments;
- Improper design of control devices (flare, scrubber) to neutralize MIC emissions caused by process upsets or failure of control systems; and
- Insufficient cooling capacity to control MIC storage temperature or failure of cooling system.

Equipment causes of accidental releases result from hardware failure such as:

- Improper materials of construction operating as catalysts of highly exothermic reactions;
- Improper materials of construction that dissolve in MIC;
- Failure of equipment, and no backup system;
- Excessive mechanical stress because of improper fabrication, construction, or installation; and
- Mechanical fatigue.

Operational causes of accidental releases result from incorrect operating and maintenance procedures or human errors, including overfilling of storage vessels, neglecting to purge process lines with nitrogen before making repairs, incomplete disaster plans, and inadequate maintenance in general.

Release Prevention and Control

To develop a thorough release prevention plan, control must be maintained over the following areas:

- Process design;
- Physical plant design;
- Protective systems; and
- Operating and maintenance practices.

Process design involves the basic chemistry of a process and how this chemistry is affected by the variables of flow, pressure, temperature, and composition. The first concern in process design is understanding how deviations from expected conditions could result in an accidental release. Any aspect of a process may be modified to enhance the integrity of the system. For example, the quantities of materials used, the pressure and temperature conditions, the type and sequence of unit operations, contro strategies, and the instrumentation used.

After the Bhopal release, for example, a joint Federal/State Task Force investigated the potential for a MIC release at the Institute, West Virginia, MIC unit. The major areas measured for this study were:

- Whether the process design prevented the likelihood of MIC concentration;
- Whether there was sufficient cooling o MIC in process vessels;
- Whether MIC inventory was minimized and
- Whether sufficient instrumentation and monitoring were provided for early detection of possible process upsets.

Physical plant design involves equipment, siting and layout, and transfer/transport facilities. Because o the extreme reactivity of MIC it shoul always be handled and stored in a protective environment. Many metals such as carbon steel, iron, tin, and aluminum, are commonly used by the chemical industry, but could act to catalyze a dangerously rapid trimerization of MIC UCAPCO (formally Union Carbide) recommends storing and handling MIC onl in stainless steel, types 304 and 316 nickel; and glass-lined equipment. Glass lined steel should be free of pinholes.

Of the four companies currentl producing MIC in the U.S., DuPont an Sandoz in Texas consume MIC a quickly as it is produced, making layou of the site less critical. The use o underground storage tanks at UCAPC was considered in the Task Force stud and found to be adequate with existin controls. The siting and layout of particular MIC facility is complex, requiring careful consideration of factors including: other processes in the vicinity the proximity of population centers, prevailing winds, local terrain, and the potential for flooding and other natural event Generally, large inventories of MI should be kept away from sources of fi or explosion. Vehicular traffic near MI process or storage facilities should b minimized. MIC piping should not b located adjacent to other piping und high pressure or temperature or th carries flammable materials. Storag facilities should be segregated from th main process. During an emergenc there should be multiple means of acces for emergency crews. Since all bulk shipments of MIC in the U.S. have bee eliminated, loading and unloadir facilities are no longer potential accide areas.

Protection technologies for the containment and neutralization of MIC include enclosures, scrubbers, flares, and other secondary control systems. Enclosures are containment structures that capture any MIC spilled or vented from storage or process equipment, thereby preventing immediate discharge of the chemical to the environment. Enclosures contain the spilled liquid or gas until it can be transferred to other containment, discharged at a controlled rate, or transferred at a controlled rate to scrubbers for neutralization. UCAPCO has an underground enclosure capable of collecting 42,000 gal. (159,000 L).

Scrubbers can be used to control MIC released from process vents and pressure relief discharges from storage and process equipment, Because of its extreme reactivity with caustics, MIC is destroyed rather than absorbed by a scrubber. Scrubbers used to control MIC emissions are designed to convert any emissions associated with the processing of MIC and to neutralize MIC emissions in case of a catastrophic release.

Flares are routinely used in the chemical processes to dispose of intermittent or emergency emissions of flammable waste gases. Flares used to control MIC emissions serve as a secondary or backup control; they should be designed to operate effectively during the course of a worst-case event such as the failure of the primary control device (scrubber).

Other control techniques currently in service for reducing possible releases of MIC *include carbon adsorption and vapor* incineration.

If an accidental release occurs, mitigation technologies can reduce the consequences. Such measures include physical barriers, water sprays and steam curtains, activated carbon for liquid spills, and evacuation. The purpose of a mitigation technique is to divert, limit, or disperse the spilled or released chemical.

Since accidental releases of toxic materials result not only from inadequate process design or equipment failure, but also from deficiencies in operation and maintenance, the safe operation of plants processing MIC requires competent and experienced managers end staff. Employees should be fully trained in the important aspects of handling MIC, in potential hazards, and in cleanup and emergency procedures. Well-defined procedures can decrease the possibility *of a hazardous release and reduce the* magnitude of any release that occurs.

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The complete report, entitled "Prevention Reference Manual: Chemical Specific, Volume 13: Control of Accidental Releases of Methyl Isocyanate," (Order No. PB 89-1161 483/AS; Cost: $15.95, subject to change) will be available only from:

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