PRELIMINARY SURVEY REPORT:

CONTROL TECHNOLOGY FOR CHEMICAL PROCESS UNIT OPERATIONS

AT

Ciba Geigy Corporation
Toms River, New Jersey

REPORT WRITTEN BY:

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NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
Division of Physical Sciences and Engineering
Engineering Control Technology Branch
4676 Columbia Parkway
Cincinnati, Ohio 45226

PLANT SURVEYED:	Ciba Geigy Corporation Toms River, New Jersey
SIC CODE:	Group 281, 2815
SURVEY DATE:	July 19, 1983
SURVEY CONDUCTED BY:	Harold Van Wagenen C.K. Wang
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ANALYTICAL WORK PERFORMED BY:	None Performed

I. INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) is conducting a study titled "Occupational Hazard Control Options for Chemical Process Unit Operations." Objective is to obtain and disseminate information on principles, equipment, and techniques employed in the chemical processing industries to minimize or eliminate worker exposure to hazardous compounds. This project is being conducted by NIOSH personnel on an in-house basis.

Preliminary site visits are made to a number of chemical processing facilities to obtain information on effective control technology. Later in-depth studies, which may include area and personal monitoring, and monitoring of emission sources for specific materials, will be conducted on a minority of these facilities--selected on the basis of the effectiveness of controls observed during preliminary site visits.

The reports from these surveys are then used as a basis for preparing technical reports and journal articles on effective hazard control measures. The information from these research activities builds the data base of publicly available information on hazard control techniques for use in preventing occupational exposure to hazardous chemicals.

This report covers the preliminary site visit (July 19, 1983) to the Ciba Geigy Corporation complex at Toms River, New Jersey. Ciba Geigy's Chemicals and Dyestuffs Division employs phosgene ($COCl_2$) in producing a group of dyestuffs sold to the carpet and textile industries. This visit concentrated on the control technology employed during receipt, transfer, and reactions of phosgene.

II. PLANT AND PROCESS DESCRIPTION

Two Ciba Geigy divisions (Chemicals and Dyestuffs, and Plastics and Additives) have both R and D and extensive manufacturing facilities at this park-like site. The huge complex is located on 1,250 acres of company-owned pine woods. It is reached by State Route 37 and is approximately five miles west of the New Jersey seacoast town of Toms River. The first buildings in the complex date back to 1951, with later additions of multi-story buildings. Due to the past recession, the work force has been trimmed to about 1,000 persons from a high of approximately 1,300. The Oil, Chemical, and Atomic Workers (OCAW) have represented the hourly workers for the past decade. The Chemicals and Dyestuffs Division makes a large number of individual dyestuffs by batch operation of many 6,000- and 4,500-gallon, rubber-lined reactors located in three separate multi-story buildings. Most reactions are conducted in water. Generally, the dyestuffs reactions are conducted at low temperatures (below 50°C), under negative vent, for reaction periods of 12 to 48 hours. From the reactors (located on the second story of these buildings), the individual batch slurries are blown to plate and frame filter presses, and cake drying in batch vacuum dryers. Finally, the individual dry batches are transported in drums to a large finishing building, where they are milled and ground, standardized, and packed in fiber drums.

With the exception of the highly hazardous phosgene, the other chemicals employed in water slurry dyestuff reactions are considered relatively innocous, according to Ciba Geigy toxicology investigations. The phosgenation reaction is the final reaction in a sequence of three, leading to production of the specific dyestuff observed by NIOSH personnel. The sequence of reaction steps is: 1) reaction of amine with nitrous acid to form a diazo compound, 2) coupling of the diazo compound to form an intermediate, and 3) phosgenation of the intermediate (phosgene is slowly introduced under the water slurry surface via a stainless steel nozzle into a high shear agitation zone).

Phosgene has an 8-hour PEL value of 0.1 ppm (approximately 0.4 mg/m^3). Inhaled in the lungs, phosgene ($COCl_2$) decomposes to form carbon monoxide and hydrochloric acid. The acid liberation leads to pulmonary edema, bronchopneumonia, chronic lung disease, and death when exposure has been severe. Because phosgene was a World War I chemical warfare gas, it presents a psychological as well as a physiological control problem.

The phosgene receipt, storage, and handling area is in a separate, isolated building. Phosgene is received in a special truck load assembly of very large cylinders, each weighing approximately 3,500 pounds gross, and 2,000 pounds net. The cylinders needed for about a week's production are stored within the windowless building and are moved around inside by means of monorail and hoist mechanisms. Two active cylinders rest on parallel scales and protrude through the walls of the building into what is essentially a huge covered glove box. The operators, using the attached gloves, reach into the sealed box to make connections to plant piping (using special tools to connect flexible hoses and connectors to cylinder fittings). Nitrogen, also supplied from a bank of cylinders, pushes the liquid phosgene from the cylinders through the inside pipe of a double pipe assembly to the reactors via rotometers mounted on a control panel board. Phosgene flow rates through the rotometers are regulated by remotely controlled feed line valves. The panel board itself is completely surrounded by a plastic enclosure hooked up to the Rotoclone[R] ventilation system. The annular space between the inner stainless steel and outer carbon steel pipes is monitored for phosgene leaking from inner pipe by use of a Congo Red solution. During 25 years of operation, on a 24-hour shift work basis, there has never been a phosgene leak in this line, nor any indication that the dry phosgene has caused stainless steel stress cracking. However, Ciba Geigy has had to replace the stainless steel piping used to introduce the phosgene under the surface of the water slurry inside the 6,000-gallon reactors. These reactors are rubber lined and equipped with 1) a high speed Lightening[R] agitator to maintain high shear agitation at point of phosgene entry, 2) a central slow speed sweep agitator to turn over the viscous water slurry, 3) a caustic scrubber using a venturi system to produce vacuum and wash the phosgene from the exhaust before releasing into the Rotoclone[R] system, 4) an effective pH metering unit, 5) an ultrasonic foam detector, and 6) packed gland agitator seals using Garfite 100 packing.

III. CONTROLS

Summary

Occupational exposures can be controlled by the application of a number of well-known principles, including engineering controls, work practices, personal protective equipment, and monitoring. These means may be applied at or near the hazard source, to the general workplace environment, or at the point of occupational exposure to individuals. Controls applied at the source of the hazard, including engineering controls (material substitution, process/equipment modification, isolation or automation, local ventilation) and work practices, are generally the preferred and most effective means of control for both occupational and environmental problems. Controls which may be applied to hazardous emissions dispersed in the workplace environment include dilution ventilation, dust suppression, and housekeeping. Control measures which should be applied near individual workers, include the use of remote control rooms, isolation booths, work practices, and personal protective equipment.

In general, a system comprised of the above control means is required to provide worker protection under normal operating conditions as well as under conditions of process upset, failure, and/or maintenance. Process and workplace monitoring devices, personal exposure monitoring, and medical monitoring are important mechanisms for providing feedback concerning the effectiveness of the controls in use. Ongoing monitoring and maintenance of controls to ensure the proper use and operating conditions, and the education and commitment of both workers and management to occupational health are also important ingredients of a complete, effective, and durable control system.

These principles of control apply to all situations, but their optimum application varies from case-to-case. In the case of phosgene at the Ciba Geigy Toms River plant, isolation of the phosgene storage area and many of the operating procedures are aimed at keeping this hazardous material away from plant personnel. Others are intended to minimize fear and to promote confidence in the system and systematic adherence to the operating procedures. There are many safety devices and procedures which will now be described.

Engineering Controls

Isolation is the engineering principle followed in the location of the phosgene cylinder receipt, storage, and handling building. Both the building interior and the handling enclosure are automatically vented by local exhaust ventilation to a potassium hydroxide scrubber. The approximately 600-foot phosgene feed line from the phosgene supply cylinders to the totally enclosed reactor control board provides a pipe within a pipe protection. In turn, the reactors and the reactor control panel have a high capacity local exhaust ventilation (Rotoclone^{R}) system. This continuously vents through a caustic scrubber to eliminate the residual unreacted gaseous phosgene from entering the atmosphere.

In handling liquid phosgene: 1) piping and fittings are 316SS, 2) ball valves are 316SS with Teflon seats, 3) flexible hoses have Teflon inner cores and 316SS overbraid, 4) pressure gauges are 316SS with tantalum diaphrams, and 5) gaskets (employed only where absolutely necessary) are encapsulated asbestos. Such asbestos gaskets are present in the phosgene flange entry point at the top of each phosgene reactor. Flange covers (connected to the rotoclone local exhaust duct) are fitted around the flanged joints to contain phosgene in the event of a flange failure.

Monitoring

At the phosgene storage building and enclosure, MDA phosgene analyzers continuously monitor and record phosgene levels. Two separate MDA analyzers are mounted in the enclosure and connect to separate alarm systems. The first, monitoring the enclosure air, indicates in a 0-0.4 ppm range and alarms at 0.1 ppm. This alarm alerts the production office, automatically closes the phosgene supply valves, turns on scrubber, and actuates flashing amber lights along the adjacent roadways. The other analyzer monitors the scrubber exhaust stream, indicates in a 0-16 ppm range, and alarms at a 2.5 ppm level. Its alarm system alerts the personnel in the production office, the reaction area, main gate house, and adjoining buildings (which are evacuated), activates roadway flashing red lights, and closes phosgene supply line valves situated both at the phosgene enclosure and the panel board.

Two similar MDA phosgene analyzers are located in the production office. Both analyzers monitor the area above the phosgene reactors. The 0-0.4 ppm analyzer is set to alarm at 0.1 ppm and evacuates the building. The 0-16 ppm analyzer for monitoring releases above 0.4 ppm.

With reactors operating under substantial vacuum, the only likely leakage of phosgene from the reactor to the working area is occasioned by foam rising in the reactor, and partially blocking the vacuum vent line to create a positive pressure. To prevent this occurrence, there is an automatic addition of anti-foam agent when foam rises above a certain level in the reactor. The automatic addition of anti-foam agent is triggered by ultra-sonic foam detectors mounted on the reactor walls. Because of the vacuum, both agitators in each reactor are equipped with simple packed glands-filled with Garfite 100 packing.

To guard against the remote event that prowlers might scale the perimeter fencing, the phosgene building doors and the front of the attached enclosure are protected by infra-red personnel sensors. These activate an alarm in the manufacturing office and main gate house if unauthorized personnel approach.

Personal exposure monitoring for phosgene is practiced by all employees working in both the phosgene reactor and storage area. A detailed written log is kept in the production office of times when personnel enter and leave these areas. During the periods the operators are within these areas, they wear GMD phosgene gas monitoring dosimeters. Each dosimeter, rated for 24-hour exposure, is worn by three successive shift operators doing the same job and then turned into the foreman at the end of the 24-hour period.

Medical monitoring for the operators potentially exposed to phosgene is no different than for all plant personnel. Ciba Geigy has a mandatory yearly program of blood testing and X-rays. A complete physical exam is offered on a yearly basis. Originally mandatory, it was made voluntary when some employees objected to being subjected to a mandatory general physical exam.

Work Practices and Training

The Ciba Geigy phosgene operations manual includes detailed descriptions and correct procedures for all operations involving phosgene: i.e., 1) cylinder handling, 2) phosgenation operation, 3) starting and shutdown, 4) plant-wide disaster plan, including systematic evacuation, and 5) preventative maintenance programs specifically planned and conducted to safeguard against equipment emissions and/or failure.

Because of the hazardous nature of phosgene, the operators at the various department locations never work alone. There are always two operators assigned to a specific work area with each providing backup for the other. To ensure that all workers presence at work stations and activities are constantly monitored, the production office has an elaborate TV monitoring setup. TV pictures cover the phosgene storage building and its front enclosure. Also graphically presented at the monitoring station are 1) the phosgenation reaction conditions; temperature, pressure, etc., 2) the MDA analyzer readings, and 3) the week-long recording charts of phosgene content in the air sampled above the various reactors. When entering or leaving any specific work area, the operators activate or turn off push buttons which control remote lights at the monitoring station in the plant production office.

Personal Protective Equipment

Besides the normal work clothes, Ciba Geigy also furnishes and requires the wearing of helmets, safety shoes, and safety glasses while the operators are on the job. The operators in the phosgene storage building and enclosure always wear air supplied respirators whenever handling cylinders within the building or while connecting or disconnecting cylinders in the enclosure.

IV. CONCLUSION AND RECOMMENDATIONS

Our inspection disclosed that all elements seen were of a high order--personnel, equipment, operating standards, monitoring, and work practices including housekeeping. Awareness of both safety and occupational health hazards was strong. This installation may warrant an in-depth survey both because of numerous sophisticated control technology features, and the cooperative attitude of the company personnel.