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WALK-THROUGH SURVEY REPORT:

CONTROL TECHNOLOGY FOR CHEMICAL BATCH UNIT OPERATIONS

AT

Mobil Chemical Company
Charleston Heights, South Carolina

REPORT WRITTEN BY:

Charleston C. K. Wang

REPORT DATE:

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101-22

NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
Division of Physical Sciences and Engineering
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16. Abstract (Limit: 200 words)

A walk through survey was conducted to assess a phosphorus products manufacturing facility at Mobile Chemical Company (SIC-2819), Charleston, South Carolina in December 1983. The facility produced phosphorus-trichloride (7719122) (PT). The primary engineering control was a water scrubber to remove PT vapors from gas streams moving at 1000 to 5000 cubic feet per minute. The acidic solution resulting from the scrubber operation was neutralized by sodium-hydroxide and then sent for waste water treatment. Double mechanical seals were used to prevent PT leaks from pumps, valves, and piping. All storage tanks were constructed of nickel coated steel. Sampling ports for product quality control were equipped with ventilated sample hoods. Ambient air was continuously monitored for hydrogen-sulfide (7783064) and organophosphorus compounds. Five percent of the finished product was stored in 50 gallon plastic drums in a partially enclosed shed, and was then shipped. Workers were required to wear respirators, protective outer garments, and gloves. Eye washers and safety showers were available. Monthly safety meetings were held. The author concludes that the facility has adequate, though not outstanding, control technology. The drumming operation poses a potential exposure hazard due to its being labor intensive.

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PLANT SURVEYED:	Mobil Chemical Company Chemical Products Division King Street Extension P.O. Box 70339 Charleston Heights, South Carolina 29415
SIC CODE:	2819
SURVEY DATE:	December 9, 1983
SURVEY CONDUCTED BY:	Charleston C. K. Wang Phillip A. Froehlich
EMPLOYER REPRESENTATIVES CONTACTED:	Charles T. Ferraro, Corporate Industrial Hygienist J. Herman Schulte, P.E., Manager of Environmental Control David Stack, Safety Engineer
EMPLOYEE REPRESENTATIVES CONTACTED:	None Plant is represented by: United Steelworkers of America Local 863 P.O. Box 6006 Myers Branch Charleston, South Carolina 29405

I. INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) is the primary Federal agency engaged in occupational safety and health research. Located in the Department of Health and Human Services (formerly DHEW), it was established by the Occupational Safety and Health Act of 1970. This legislation mandated NIOSH to conduct a number of research and education programs separate from the standard setting and enforcement functions carried out by the Occupational Safety and Health Administration (OSHA) in the Department of Labor. An important area of NIOSH research deals with methods for controlling occupational exposure to potential chemical and physical hazards. The Engineering Control Technology Branch (ECTB) of the Division of Physical Sciences and Engineering has been given the lead within NIOSH to study the engineering aspects of health hazard prevention and control.

Since 1976, ECTB has conducted a number of assessments of health hazard control technology on the basis of industry, common industrial process, or specific control techniques. Examples of these completed studies include the foundry industry; various chemical manufacturing or processing operations; spray painting; and the recirculation of exhaust air. The objective of each of these studies has been to document and evaluate effective control techniques for potential health hazards in the industry or process of interest, and to create a more general awareness of the need for or availability of an effective system of hazard control measures.

These studies involve a number of steps or phases. Initially, a series of walk-through surveys is conducted to select plants or processes with effective and potentially transferable control concepts or techniques. Next, in-depth surveys are conducted to determine both the control parameters and the effectiveness of these controls. The reports from these in-depth surveys are then used as a basis for preparing technical reports and journal articles on effective hazard control measures. Ultimately, the information from these research activities builds the data base of publicly available information on hazard control techniques for use by health professionals who are responsible for preventing occupational illness and injury.

This report covers the preliminary site visit (December 9, 1983) to the phosphorus products manufacturing plant of Mobil Chemical Company in Charleston, South Carolina. The visit focused on the phosphorus trichloride process and on the control technology employed in the manufacturing and shipping of phosphorus trichloride.

II. PLANT AND PROCESS DESCRIPTION

The Mobil Chemical Company plant is located on the Ashley River in Charleston, South Carolina. The plant is reached via the King Street Extension. During the 1860's, this site was originally used for manufacturing phosphate fertilizers. In 1929, the site was merged into one company, the Virginia-Carolina Chemical Company. Mobil purchased the site from the Virginia-Carolina Chemical Company in 1963. The plant manufactures a variety of organic phosphorus compounds, including alkyl phosphites, alkyl phosphonates, organic acid phosphates, organic pyrophosphoric acids, flame retardants, corrosion inhibitors, extractant agents, and inorganic phosphorus compounds including phosphorus trichloride, phosphorus oxychloride, and orthophosphoric acids. There were four organic processing buildings where 40 to 50 different products are manufactured, usually six at any one time. The organic processes are 75% continuous facilities. There are three outdoor inorganic chemical manufacturing areas. The inorganic processes are essentially continuous.

As the plant no longer (since 1970) makes elemental phosphorus, it is purchased for delivery in railway tank cars. The elemental phosphorus is shipped as a liquid (M.P. 114°F) under water. Barge transportation ceased in 1941.

The plant visit concentrated on the phosphorus trichloride process. Phosphorus trichloride is made by the chlorination of elemental phosphorus:

$$P_4 + 6\ Cl_2 \quad = \quad 4PCl_3$$

Liquid phosphorus is pumped into the process from the unit storage/holding area. Finished product is stored in steel tanks lined with nickel or other inert materials of construction. The PCl_3 unit shares operators with the $POCl_3$ and the phosphoric acid units. These units employ four (4) operators and one (1) supervisor per shift. The three units operate on a 24-hour, 3-shift basis.

Health Hazard Information

Phosphorus trichloride is a colorless to yellow fuming liquid with a sharp irritating odor similar to hydrochloric acid. It affects the body through inhalation, ingestion, and skin or eye contact. It is a severe irritant to eyes and can cause burns to skin. Inhalation causes irritation of the respiratory tract. Repeated inhalation causes chronic cough and wheezing.

The current OSHA standard for PCl_3 is 0.5 ppm of phosphorus trichloride in air, averaged over an 8-hour work shift (equivalent to 3 mg/m^3 of PCl_3 in air).

III. CONTROLS

PRINCIPLES OF CONTROL

Occupational exposures can be controlled by the application of a number of well-known principles, including engineering measures, work practices, personal protection, and monitoring. These principles 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 measures (material substitution, process/equipment modification, isolation or automation, local ventilation) and work practices, are generally the preferred and most effective means of control both in terms of occupational and environmental concerns. Controls which may be applied to hazards that have escaped into the workplace environment include dilution ventilation, dust suppression, and housekeeping. Control measures may also be applied near individual workers, including the use of remote control rooms, isolation booths, supplied-air cabs, work practices, and personal protective equipment.

In general, a system comprised of the above control measures 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 effectiveness of the controls in use. Ongoing monitoring and maintenance of controls to insure 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. The application of these principles are discussed below.

The Control Technology

The phosphorus trichloride manufacturing process is an open air unit consisting of the reactor, column, condensers, and various storage tanks.

The primary environmental/safety and health control unit operation is the Norton* Cyclsandire water scrubber (water scrubbing on colum packing) for removing PCl_3 vapors from gas steams:

$$PCl_3 + 3H_2O = H_3PO_3 + 3\ HCl$$

A dilute phosphorous/hydrochloric acid solution results from the scrubbing reaction and this is neutralized with caustic prior to being sent for waste water treatment. Figure 1 gives a diagram of the scrubber. Odor problems do arise in the organic areas. The scrubber body is of polyvinyl chloride or fiberglass construction.

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* Norton no longer manufactures scrubber equipment.

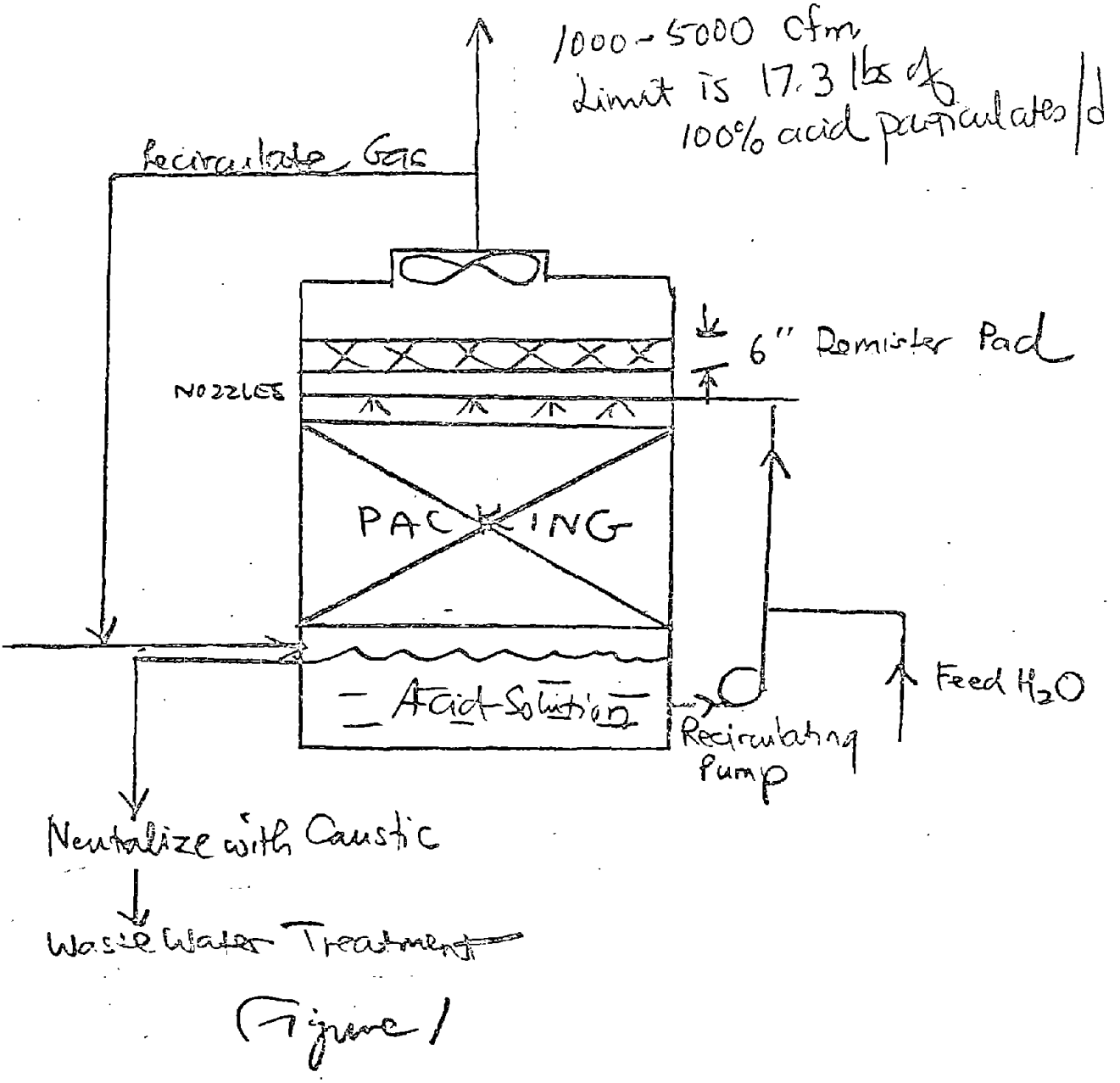
1000 - 5000 cfm
Limit is 17.3 lbs of 100% acid particulates/d
Recirculate Gas
6" Demister Pad
NOZZLES
PACKING
Acid Solution
Recirculating Pump
Feed H_2O
Neutralize with Caustic
Waste Water Treatment

Figure 1

The plant has found that the PCl_3 may auto-ignite if insufficient water is used, this being caused by the release of gaseous phosphines.

Another control involves the prevention of PCl_3 leaks from pumps, valves, and piping. Double mechanical pump seals and completely enclosed canned pumps are used. No stuffing boxes are used on pumps. Valves are constructed of nickel with teflon plugs. Diaphragm valves are preferred. Control valves have bellow seals. Piping is all welded nickel. Flange joints may be used. Some extra heavy welded carbon steel piping with flange joints is also used.

In the storage area, the tanks are constructed of nickel clad steel. Although glass is also a good material of construction for handling PCl_3, it is not used because of the threat of acid corrosion from the outside of the tank. If phoshorus trichloride is spilled on the external steel casing, hydrogen is generated and this gas penetrates into the inside of the tank and spalls (pops) the inside glass lining. Tanks are enclosed by spill retaining walls made of concrete. Critical valves in these pit areas around tanks have handle extensions which allow the valves to be operated from outside the pit.

We also surveyed the drumming operation. While only 5% of the finished product is drummed (the rest being shipped via tank cars, trucks, or internal use pipeline), the drumming operation is relatively labor intensive and presents a potential for exposure if inadequately controlled. Fifty-gallon plastic drums are filled with the use of a special ventilated feeding lance. The drums are moved manually on roller tracks to and from the filling lance. The drumming is performed in a semi-enclosed shed.

Truck loading is accomplished with two operators. Dedicated trucks an independent contractor are used. Loading is performed with the truck driver out of cab, but within 25 feet and in sight of the truck.

Another interesting unit operation surveyed is product quality control sampling. The PCl_3 operator takes quality control samples about one every 2 hours. A ventilated sample hood is used to capture and remove PCl_3 emissions. An aspirator is used to draw PCl_3 samples from the process line into glass reservoir. Nitrogen pressure is used to return excess PCl_3 and a continuous nitrogen purge is used to keep lines from plugging.

Operators wear respirators, protective outer garments, and gloves. Eye washes and safety showers are available on site. These equipment are checked regularly at the beginning of each shift. Safety precautions and equipment operation methods are reviewed regularly between the operators and the supervisor. Informal safety refreshers are conducted by the shifts. Monthly safety meetings where worker input is encouraged are held.

The South Carolina State OSHA inspected the plant in May 1982. Five samples were taken from the PCl_3 area. Four were nondetectable and 1 showed a "trace" of PCl_3.

The plant takes about 90 samples per year and follows internal industrial hygiene limits. Every new process is evaluated by sampling. Personal industrial hygiene data is computerized.

Continuous monitoring of workplace air contaminants is available in the following arrangement:

1) Two monitors for H_2S in the phosphoric acid filter press room.

2) A monitor in the organophosphorus area analyzes for three to four different organic chemicals at four locations every hour.

Conclusions/Recommendations

On the whole, the PCl_3 unit has adequate control technology. However, none of the controls observed appeared to be exemplary. The PCl_3 drumming operation may merit further study, as the potential for worker exposure is always higher where labor intensive operations occur, and any good control technology documented may benefit similarly hazardous operations.