CONTROL TECHNOLOGY ASSESSMENT
OF CHEMICAL PROCESSES

Tennessee Eastman Company
Kingsport, Tennessee

Preliminary Survey Report
for the Site Visit of
September 2, 1981

Contract No. 210-80-0071

February 2, 1982

Submitted to:

Harold Van Wagenen, Project Officer
National Institute for Occupational
Safety and Health
4676 Columbia Parkway
Cincinnati, Ohio 45226

Submitted by:

Julius H. Bochinski, Program Manager
Enviro Control, Inc.
The Dynamac Building
11140 Rockville Pike
Rockville, Maryland 20852

REPORT NO.:
ECTB 101-12a

TABLE OF CONTENTS

I. INTRODUCTION

A. Summary of Visit

The Kingsport, Tennessee Plant of the Tennessee Eastman Company was visited by representatives of Enviro Control, Inc. to conduct a preliminary survey of the techniques used to control worker exposure to hazardous substances. Participants included:

Tennessee Eastman Company

W.A. McGee	Manager, Industrial Hygiene
E.H. Clower	Superintendent, Hydroquinone Plant
E.F. Lawrence	Sr. Industrial Hygienist
M.G. Schurger	Industrial Hygienist
J. Skillen	Sr. Chemical Engineer, Acid Concentration Dept.
J.R. McDonough, MD	Medical Director

Figure 6 (in the Appendix) illustrates the organizational structure of the company's Medical Department and the eight man Industrial Hygiene Group in the department.

National Institute for Occupational Safety and Health

H. Van Wagenen	Project Officer

Enviro Control, Inc.

J.H. Bochinski	Program Manager
S.L. Bergh	Chemical Engineer

The survey was completed in one day. It included discussions of the processes involved, inspections of the processes and associated control equipment, and detailed discussions of the control techniques of interest. This report summarizes the processes and describes in detail the control techniques observed in the hydroquinone plant and a separate liquid products drumming installation. All Tennessee Eastman personnel involved were very cooperative in providing information on the processes and associated equipment, industrial hygiene concerns, specific hazards of the chemicals involved, operator training, safety standards and evolution of control techniques.

B. Background Information on Contract

This visit was conducted as part of the Control Technology Assessment of Chemical Processes, NIOSH Contract No. 210-80-0071. The purpose of this contract is to identify and assess superior control techniques for limiting worker exposure to hazardous substances during chemical processing. This is being done through extensive visits to industrial facilities. Preliminary surveys are intended to generate information about the control strategies used at various facilities and will be used to determine which facilities warrant further, in-depth surveys. Information collected from the visits will be compiled into a control technology reference source to aid in the solution of worker exposure problems in industry . In all cases it will be noted that control techniques cannot be extrapolated to other situations without careful evaluation of all factors involved.

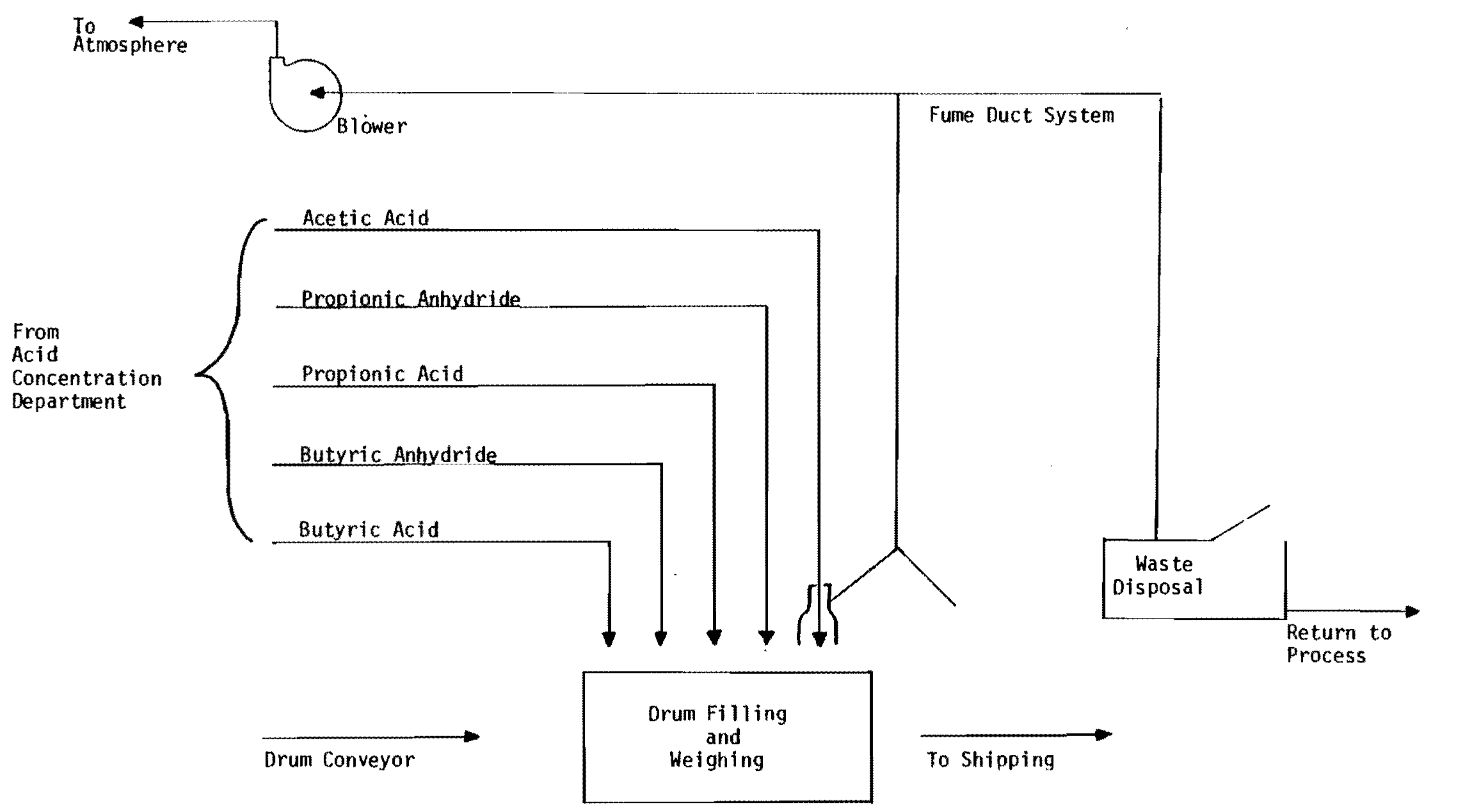
II. PLANT AND PROCESS DESCRIPTION

The Kingsport Plant is a very large facility producing a myriad of different products. This survey was only concerned with the control techniques used in the Hydroquinone Plant and the drumming facilities for the Acid Concentration Department. The following sections describe the processes involved and briefly discuss important control techniques observed.

A. Acid Concentration Drumming Facilities (see Figure 1)

The Acid Concentration Department produces several organic acids and anhydrides through distillation and purification of various

Figure 1. Drum Filling and Fume Control System Schematic



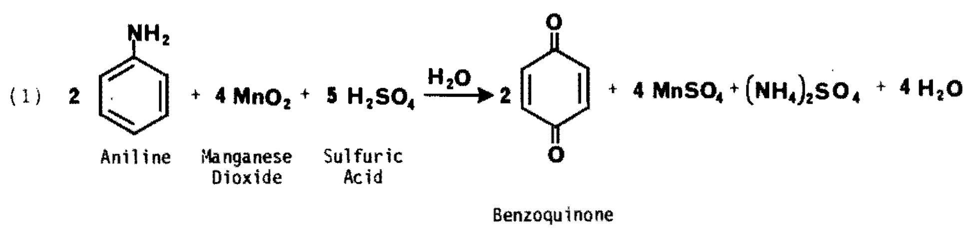
POTENTIALLY HAZARDOUS CHEMICALS INVOLVED

Agent	PEL	Chemical and Physical Properties		Health Hazard: Route of Entry	Health Hazard: Effect
Acetic Acid	10 ppm	M.P.	52° F	Inhalation	Irritant
		B.P.	244° F	Contact	
		V.P.	11mm		
		Solubility	Miscible		

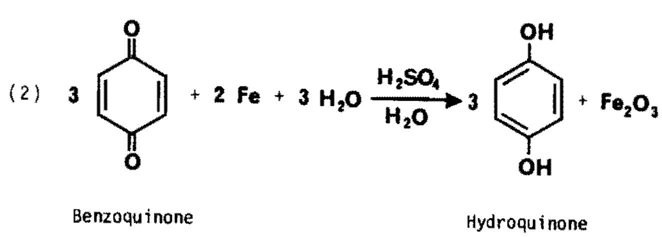
streams from throughout the plant. Different grades of acetic acid, propionic acid, propionic anhydride, butyric acid and butyric anhydride are produced for shipment to outside customers in both top and side loading drums. To minimize possible worker exposure to these chemicals during drum filling a special fume control system has been installed. The fume control system is discussed in more detail in Section III, A.

B. <u>Hydroquinone (see Figure 2)</u>

In essence, the hydroquinone process is a three-step operation. In the first step aniline is oxidized to benzoquinone, or quinone, in the presence of excess manganese dioxide and sulfuric acid as shown in Reaction 1.



In the next step benzoquinone is distilled from the reaction liquor and contacted with a water suspension of iron to reduce it to hydroquinone as shown in reaction 2.



The final step involves purification of the hydroquinone to the quality desired.

Figure 2. Hydroquinone Manufacture

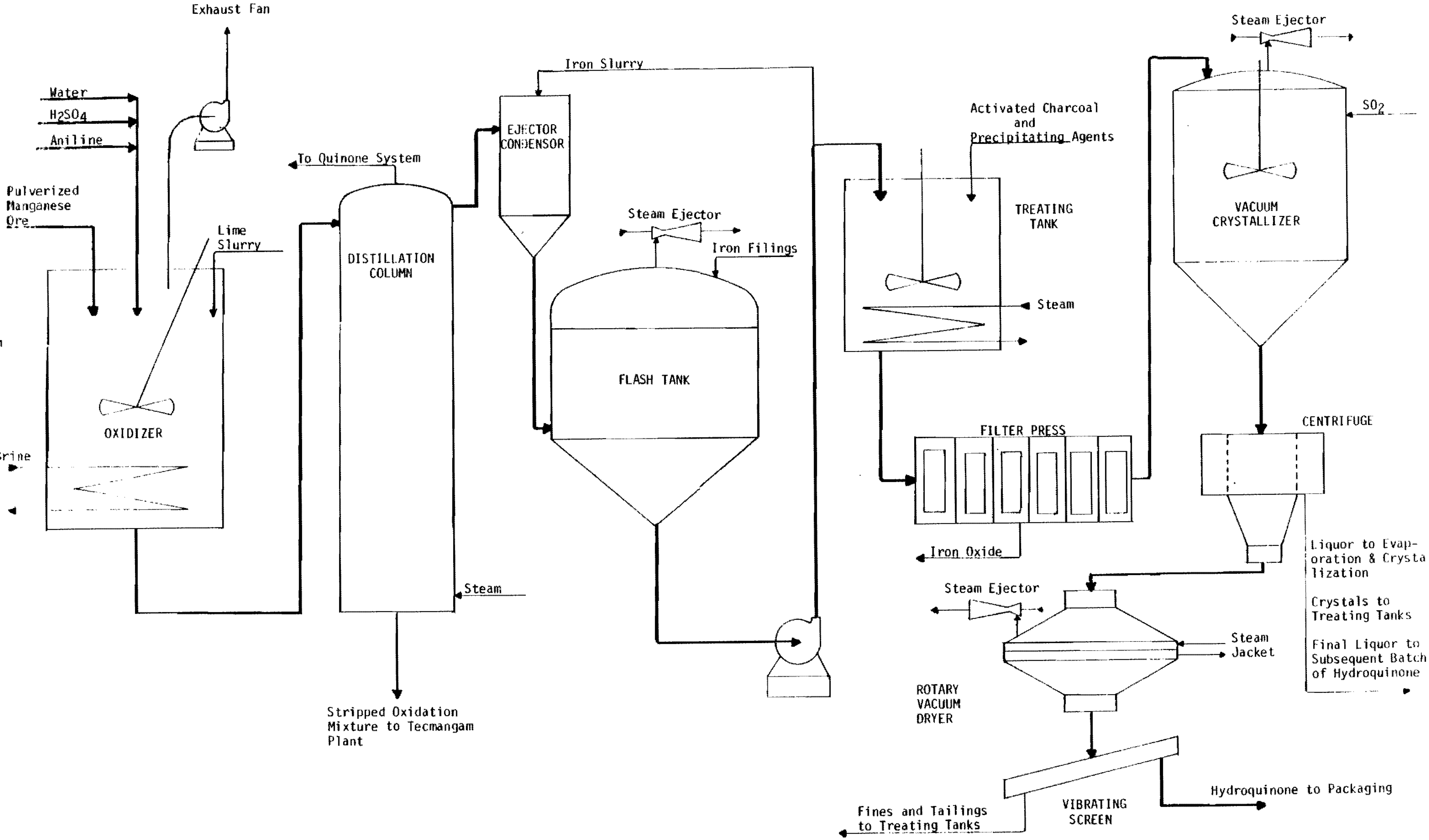


Table 1. HYDROQUINONE PROCESSING

Potential Emission/Exposure Points	Control Techniques
• Plate-and-Frame Filter Presses • Removal of Cake from Centrifuges	• Isolated Rooms for Presses with Local Ventilation • Centrifuges with Automatic Dumping Capability

POTENTIALLY HAZARDOUS CHEMICALS INVOLVED

			Health Hazard	
Agent	PEL	Chemical and Physical Properties	Route of Entry	Effect
Aniline	5 ppm	M.P. 21° F B.P. 364° F Solubility 3.5% V.P. 0.6mm	Inhalation Absorption Ingestion Contact	Methemeglobin Former
Hydroquinone	2 mg/m^3	M.P. 338° F Solubility 7% V.P. <0.001mm	Inhalation Ingestion Contact	Irritant
Benzoquinone	0.1 ppm	M.P. 235° F Solubility 1.5% V.P. 0.1mm	Inhalation Ingestion Contact	Irritant
Sulfuric acid	1 mg/m^3	M.P. 37° F B.P. 518° F V.P. <0.001mm Solubility Miscible	Inhalation Ingestion Contact	Irritant

Conversion of aniline to benzoquinone takes place in large wood-stave cylindrical vessels called oxidizers. There are several oxidizers which operate batchwise, but in sequence, to produce a continuous feed to the next portion of the process. Aniline, water, sulfuric acid and pulverized manganese dioxide are added to the oxidizers in both specific quantities and sequence. The mixture is agitated to keep the manganese dioxide in suspension. Because the reaction is exothermic the oxidizers have cooling coils through which a refrigerant is circulated to control the temperature of the mixture. From 4 to 24 hours later (depending on the grade of manganese ore used) the reaction reaches a set yield. Next the acidity of the mixture is reduced by addition of a hydrated lime slurry. The resultant mixture is then pumped from the oxidizers to the distillation feed tanks.

The oxidizers do not present a significant worker exposure problem. Addition of all raw materials is done through permanent connections. Though the oxidizers are not completely sealed, emission of vapors is prevented by drawing a slight vacuum on the vessel with an exhaust fan. After a batch is dumped to the distillation feed tanks the vessel is steam-cleaned through a doorway on top. To minimize worker exposure to any internal vapors, cleaning time is limited to 2 minutes.

The mixture from the distillation feed tanks is continuously pumped to the top of a distillation column. Steam is introduced at the bottom to strip the benzoquinone from the oxidizer mixture and carry it out the top as a vapor to the next stage of the process. The benzoquinone may be diverted at this point for processing into a saleable product. The stripped oxidation mixture from the bottom of the column is neutralized and filtered to produce a technical grade manganese sulfate, called Tecmangam®, used in fertilizers and animal feeds.

At this point the benzoquinone is reduced to hydroquinone in the reduction unit (as shown on Figure 2). This includes a cone-bottomed flash tank in series with a pump and an ejector-condensor. The flash tank is charged with an iron dust-water slurry, containing an excess of iron dust needed for the reduction, and sufficient water to dissolve all the hydroquinone to be formed. The benzoquinone-steam mixture enters the ejector where it is condensed and reduced to hydroquinone by a stream of iron-dust slurry. The resultant hydroquinone solution is then concentrated in the vacuum flash tank.

The distillation column and flash tanks present few opportunities for worker exposure. The equipment is all enclosed and operates continuously. However, the iron filings used to reduce benzoquinone to hydroquinone are handled in special equipment. They come in heavy-duty containers weighing up to one ton. The containers are dumped into a hopper above the flash tanks by a lifting device. To avoid the hazard of the containers falling on someone, the lifting device is enclosed in a small metal structure. The device will not operate until the door to the structure has been closed and locked from the outside by the operator. From the hopper the iron filings are introduced to the flash tank by a rotary valve.

The concentrated hydroquinone solution is now pumped to agitated, steam-heated, batch treating tanks where decolorizing and precipitating agents are added. The mixture is heated to dissolve all hydroquinone and then put through a steel plate-and-frame filter press to remove suspended iron and iron oxide. Plate-and-frame filters can present worker exposure problems. Accordingly, the two filters in the hydroquinone plant are given special considerations. These are discussed in Section III, B.

The filtered hydroquinone solution now enters a cone-bottomed vacuum crystallizer which operates by adiabatic cooling. Sulfur dioxide is added at this point to inhibit oxidation of the hydroquinone in the remainder of the process. The slurry from the crystallizer is then dropped into a centrifuge to separate the mother liquor from the crystals. The mother liquor is further evaporated and crystallized in separate units with the crystals returned to the treating tanks. The final mother liquor is oxidized in a subsequent batch of benzoquinone. Hydroquinone crystals from the centrifuge are dumped automatically to double-cone rotary vacuum dryers. The centrifuges are discussed in Section III, C.

When the crystals are dry they are dropped to a classification screen to separate fines and tailings from the product crystals. If the crystals will not readily fall from the dryer, a worker must open the top and punch the blockage out. Local exhaust ventilation is used at the mouth of the dryer in this situation. The classification/screening operation takes place in a fenced area underneath the dryers and can be a source of worker exposure. This is avoided by keeping the workers away from the vibrating screens. They will not operate until the operator has closed and locked the door to the fenced area.

The dry product crystals are finally packaged in fiber drums of various sizes. The filling is done in an enclosed drumming station equipped with local exhaust ventilation. Plant industrial hygienists report that the installation of the enclosed drumming station has reduced hydroquinone dust levels in the area from 20-35 mg/m^3 down to 1-4 mg/m^3.

The great care taken in all operations to avoid product contamination also serves to limit worker exposure. The plant has installed both local exhaust and general dilution ventilation throughout the process areas. Housekeeping includes hosing down most floors at least once a shift to avoid buildup of hydroquinone. Though not particularly volatile, hydroquinone left on the floor will oxidize to benzoquinone in the presence of moisture and this can be a source of atmospheric contamination.

Administrative controls and work practices are also used to limit worker exposure. These are discussed in Section III, D and E.

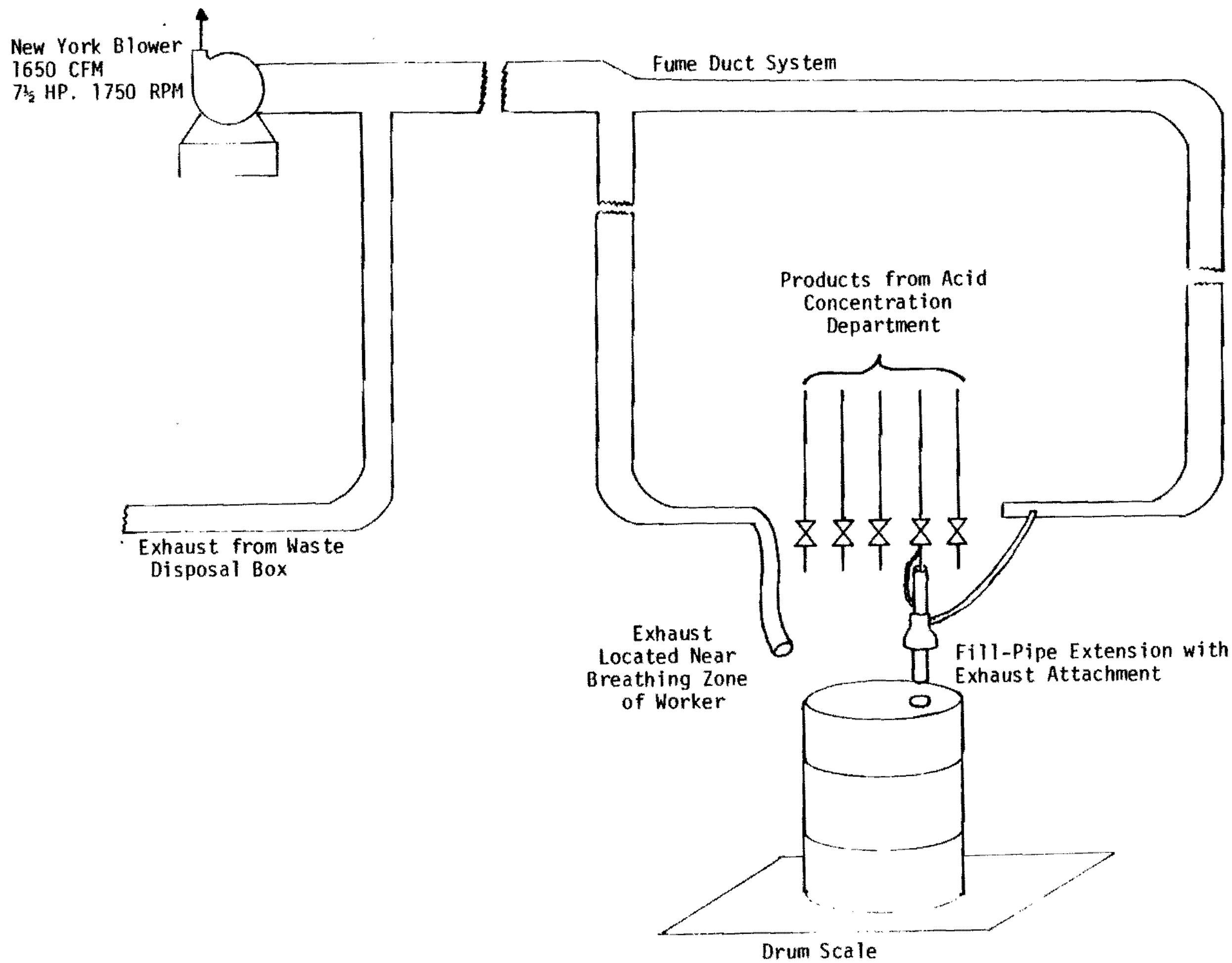
III. CONTROL TECHNIQUES

A. Drum Filling Fume Control System

Drum filling with volatile hazardous liquids has long been a source of worker exposure. The gas displaced from the drum during filling contains vapors from the liquid being filled and can cause problems for the workers involved. This situation existed in the Acid Concentration Department Drumming Facilities. To eliminate the exposure problem a fume control system was installed as shown in Figure 3. This current system is a modification to a previous fume control installation which did not perform satisfactorily. The current system appears to be very effective in reducing the amount of hazardous vapors workers are exposed to in the drum filling operation.

Fill lines for the five liquids come together in a group above a drum scale. A conveyor brings drums to the scale. A fill-pipe extension fits over the end of the line for the liquid to be filled, and into the drum. As shown in Figure 4, the fill-pipe extension consists of a section of pipe, large enough to fit over the end of the fill line and small enough to fit into the drum opening. A bell-reducer is welded to the extension so that the whole assembly rests on the drum with the pipe extending down into it. The bell reducer effectively covers the opening of the drum. A flexible hose is attached to the side of the reducer and is connected to a New York Blower through a duct

Figure 3. Fume Control System



system. When the drum is filling, displaced vapors are collected by the bell reducer and exhausted away. The fill-pipe extension is suspended from each of the fill pipes by a chain linkage and hook. Another local exhaust from the duct system is placed near the breathing zone of the operator filling the drums to draw away any other vapors which might be present. A metal waste disposal box is also connected to the blower through the duct system to enable operators to dump liquids without introducing vapors into the workplace.

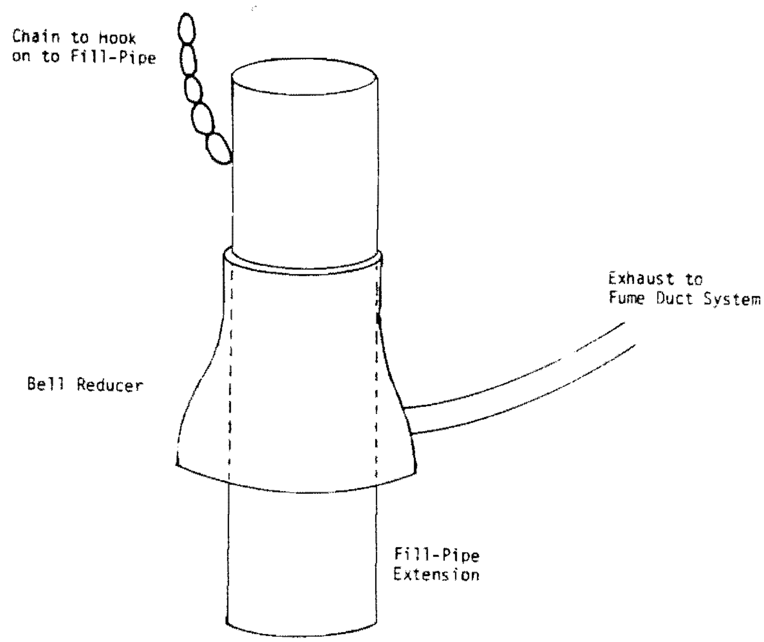


Figure 4. Fill-Pipe Extension

B. Plate-and-Frame Filter Press Rooms

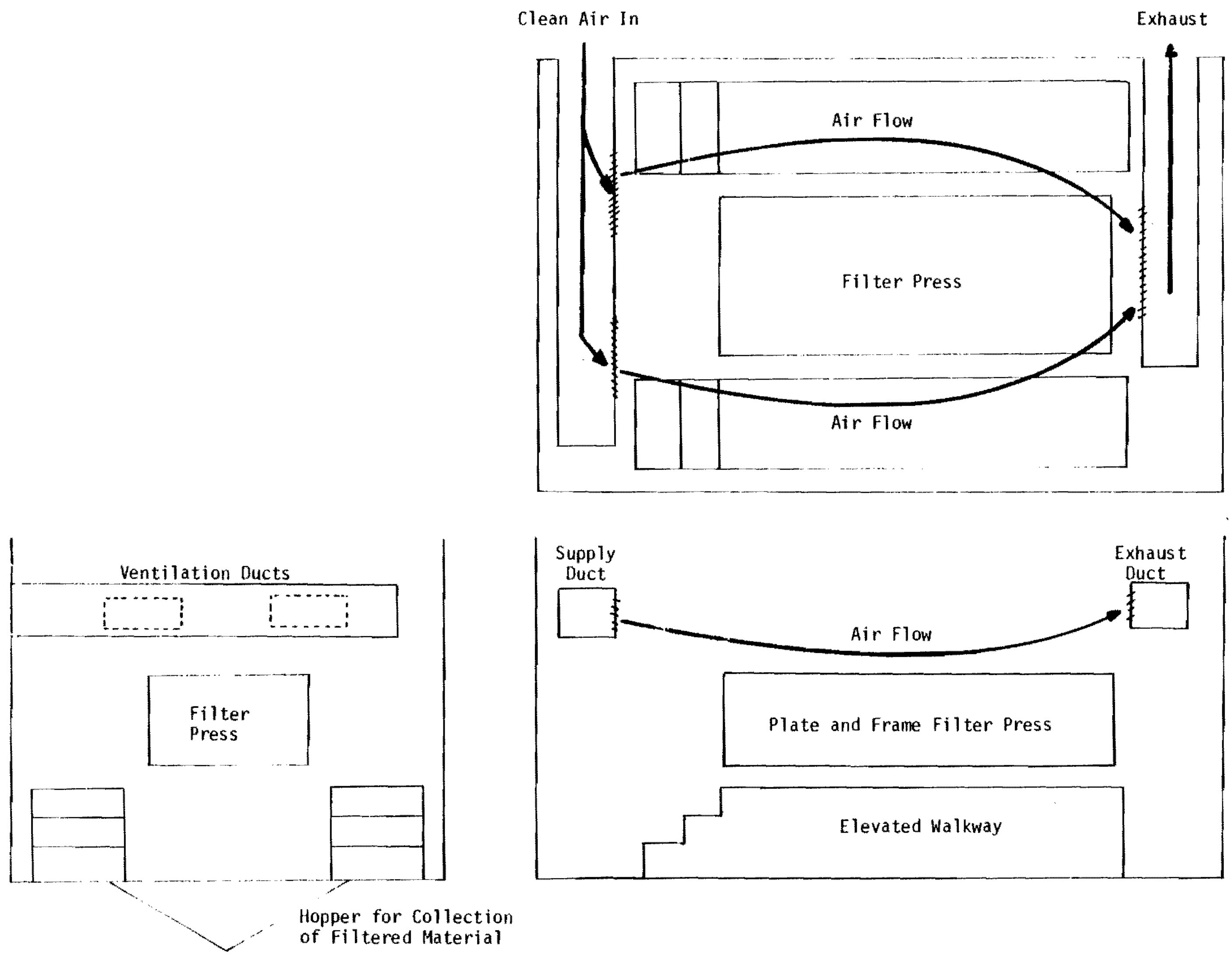
The hydroquinone slurry from the treating tanks contains iron, iron oxide and activated charcoal in suspension. The mixture is sent through a plate-and-frame filter press to remove all solids from the hydroquinone solution. Plate-and-frame filters are very difficult to keep sealed because the joints between plate-and-frame are inherent leak points. Hence, if a filter is handling hazardous substances, precautions must be taken to ensure workers are not exposed to the emissions that will generally occur.

Two presses are currently in use at the hydroquinone plant. While one press is operating the other will be shut down for cleaning. Figure 5 details the equipment layout. Each press is located in a separate enclosed room. During normal operation this keeps workers isolated from any hydroquinone emissions from the presses. Exposure is further limited by a supply ventilation system which sends air along the walkways on either side of the presses where workers will be. Operator attention to the equipment is limited to (1) a periodic water hose-down of the presses to wash away any hydroquinone crystals which may have built-up on the outside, and (2) filter-cake removal. A hopper underneath each press collects all the filtered material before it is transported away for disposal.

C. Automatic Dumping of Centrifuges

Hydroquinone crystals formed in the vacuum crystallization step of the process are separated from the mother liquor by batch centrifugation. In the past, workers had to open the top of the centrifuge and manually scrape off the cake to dump the crystals to the drying stage. This put the worker in a situation where he was in direct contact with the process materials and liable to exposure. To alleviate this potential exposure problem, the company replaced the old centrifuges with new ones. The Sharples centrifuges now in place are deisgned to automatically dump the centrifuge cake to the dryers without having an operator open them up. This was done many years ago, and it may seem

Figure 5. Plate-and-Frame Filter Press Room



like an obvious solution. However, it is a very simple and effective means of reducing worker exposure because contact with process materials at this stage is completely eliminated.

D. Administrative Controls

In addition to various engineering controls and work practices, the company has instituted administrative controls to ensure that worker exposure stays below the specified OSHA Permissable Exposure Limit (PEL) levels in the hydroquinone area. Over-exposure to hydroquinone manifests itself by a yellow pigmentation of the eye whites of the person exposed. If exposure is unchecked, the discoloration will progress and do further damage to the eye. However, the pigmentation is reversible if exposure is stopped. Workers who show signs of pigmentation are closely monitored and may be assigned to an area where contact is negligible. All workers in the hydroquinone area are periodically rotated from one job to another.

Change rooms and daily change of company furnished and laundered work clothes are provided all workers in the hydroqinone plant. In addition, daily showers on company time at end of shift are mandatory.

Worker exposures to both benzoquinone and hydroquinone are well below the OSHA PEL's. These measures are merely an adjunct to engineering controls and work practices to further reduce worker exposure.

E. Work Practices

The company has a very effective work practices program which is reflected in the excellent housekeeping throughout the plant areas. Periodic hose-down of appropriate areas helps prevent build-up of hydroquinone which would otherwise cause problems.

One of the most important considerations for the work practices program is that personal work habits are critical when handling hydroquinone. Workers who are sloppy in their approach to the chemical can generally be quickly identified by the yellow pigmentation that develops in their eye whites. Other considerations that make the program effective are:

- Training of operators and maintenance personnel: Operators are trained for each operation and task they will encounter during plant operation. It is the foreman's and Plant Superintendent's responsibility to make certain the person being trained fully understands the job procedures, modes of release of chemical substances and potential hazards involved, and control techniques to be used.

- Documented training material for each job classification: The hydroquinone plant has an extensive operator training manual which instructs the user on the safety aspects of the various jobs to be performed.

- Written plant safety standards that address:

  - Health hazards of chemicals
  - mode of emission of chemicals
  - control techniques to be used

- Corporate follow-up: Monitoring, at the operator level, the effectiveness of work practices.

APPENDIX

Additional Information from Survey

1.0 Plant Description

The hydroquinone facility is just one area of the Kingsport Plant. The entire plant consists of many different processes spread over a wide area, producing hundreds of chemicals. The plant is located on the western edge of Kingsport, Tennessee at the end of Eastman Road on either side of the Holston River. The climate in this area is warm and humid in the summer with moderately cold winters. The hydroquinone facility is housed in several multistory brick buildings. It was built in the 1930's and has not been substantially modified since then. The facility is one small part of the entire Kingsport Plant which is very large. The hydroquinone process uses 16 operators and a foreman for each of its 3 daily shifts. The entire plant employs about 13,000 workers.

2.0 Description of Programs

The Kingsport Complex has an industrial hygiene staff of eight which performs surveys on a quarterly basis for the whole facility. When a problem or potential problem is identified, the industrial hygienist makes suggestions to the appropriate operating department on how to alleviate the problem. Latest surveys indicate that workers in the hydroquinone process area are being adequately protected. Exposures to benzoquinone ranged from 0.02 to 0.09 ppm (Permissible Exposure Level of 0.1 ppm) and exposures to hydroquinone ranged from 0.1 to 1.32 mg/m^3 (PEL of 2.0 mg/m^3). Fifteen to 30 minute samples are taken in the workers' breathing zone with isopropyl alcohol impingers.

Annual apthalmological examinations including a slit-lamp corneal exam are given to all employees who may come in contact with hydroquinone. This is in addition to annual physical examinations given to all employees in the Hydroquinone Department.

The Tennessee Eastman Medical Operation is impressive. As detailed in Figure 6, ample clinical services staffing is provided for company personnel. The other major components of the Medical Department include both (1) the previously mentioned industrial hygiene group, and (2) a sizable product toxicology group. Offices, Library, and Laboratory facilities for these functional groups were well equipped.

This preliminary site visit concerned only a small portion of a huge and impressive chemical processing complex. All elements seen were of a high order - personnel, equipment, operating standards, work practices including housekeeping, scale of operation, etc. Particularly apparent was the pride of accomplishment displayed by both industrial hygienists and engineers and their close working relationship. Also noteworthy, was the candid admission by competent technical staff that: (a) engineering controls particularly did not always work effectively without major modification and testing; and (2) overall effective control employs all the technology elements stressed by NIOSH as shown by an exerpt from their presentation..."Emphasis is placed on prevention of leaks of quinone vapor, on the removal at the source by carefully designed ventilation equipment of the vapors and dusts which unavoidably escape from some operations, and on a good housekeeping program. To further minimize exposure, employees are rotated through the various operations in the department. In addition to change of uniforms each day, employees are required to take showers at the end of work each day on company time. Industrial hygiene work is being carried on continuously in relationship to hydroquinone manufacture, and regular examination of employees for ill-effects is required."

Figure 6. Tennessee Eastman Company Medical Department